

Encyclopedia of
Complexity and Systems Science Series
Editor-in-Chief: Robert A. Meyers

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Muhammad Sahimi · Allen G. Hunt
Editors

Complex Media and Percolation Theory

A Volume in the Encyclopedia of Complexity
and Systems Science, Second Edition

Encyclopedia of Complexity and Systems Science Series

Editor-in-Chief

Robert A. Meyers

The Encyclopedia of Complexity and Systems Science series of topical volumes provides an authoritative source for understanding and applying the concepts of complexity theory, together with the tools and measures for analyzing complex systems in all fields of science and engineering. Many phenomena at all scales in science and engineering have the characteristics of complex systems, and can be fully understood only through the transdisciplinary perspectives, theories, and tools of self-organization, synergetics, dynamical systems, turbulence, catastrophes, instabilities, nonlinearity, stochastic processes, chaos, neural networks, cellular automata, adaptive systems, genetic algorithms, and so on. Examples of near-term problems and major unknowns that can be approached through complexity and systems science include: The structure, history and future of the universe; the biological basis of consciousness; the integration of genomics, proteomics and bioinformatics as systems biology; human longevity limits; the limits of computing; sustainability of human societies and life on earth; predictability, dynamics and extent of earthquakes, hurricanes, tsunamis, and other natural disasters; the dynamics of turbulent flows; lasers or fluids in physics, microprocessor design; macromolecular assembly in chemistry and biophysics; brain functions in cognitive neuroscience; climate change; ecosystem management; traffic management; and business cycles. All these seemingly diverse kinds of phenomena and structure formation have a number of important features and underlying structures in common. These deep structural similarities can be exploited to transfer analytical methods and understanding from one field to another. This unique work will extend the influence of complexity and system science to a much wider audience than has been possible to date.

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Muhammad Sahimi • Allen G. Hunt
Editors

Complex Media and Percolation Theory

A Volume in the Encyclopedia of Complexity
and Systems Science, Second Edition

With 152 Figures and 16 Tables

 Springer

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Muhammad Sahimi

“To all those who have dedicated their lives to fighting colonialism, exploitation, racism, and imperialist wars.”

Allen G. Hunt

“And to those taking risks to help us against the terrors of infectious disease, like ‘doctors without borders’ and nurses everywhere.”

Series Preface

The Encyclopedia of Complexity and System Science Series is a multivolume authoritative source for understanding and applying the basic tenets of complexity and systems theory as well as the tools and measures for analyzing complex systems in science, engineering, and many areas of social, financial, and business interactions. It is written for an audience of advanced university undergraduate and graduate students, professors, and professionals in a wide range of fields who must manage complexity on scales ranging from the atomic and molecular to the societal and global.

Complex systems are systems that comprise many interacting parts with the ability to generate a new quality of collective behavior through selforganization, e.g., the spontaneous formation of temporal, spatial, or functional structures. They are therefore adaptive as they evolve and may contain self-driving feedback loops. Thus, complex systems are much more than a sum of their parts. Complex systems are often characterized as having extreme sensitivity to initial conditions as well as emergent behavior that are not readily predictable or even completely deterministic. The conclusion is that a reductionist (bottom-up) approach is often an incomplete description of a phenomenon.

This recognition that the collective behavior of the whole system cannot be simply inferred from the understanding of the behavior of the individual components has led to many new concepts and sophisticated mathematical and modeling tools for application to many scientific, engineering, and societal issues that can be adequately described only in terms of complexity and complex systems.

Examples of Grand Scientific Challenges which can be approached through complexity and systems science include: the structure, history, and future of the universe; the biological basis of consciousness; the true complexity of the genetic makeup and molecular functioning of humans (genetics and epigenetics) and other life forms; human longevity limits; unification of the laws of physics; the dynamics and extent of climate change and the effects of climate change; extending the boundaries of and understanding the theoretical limits of computing; sustainability of life on the earth; workings of the interior of the earth; predictability, dynamics, and extent of earthquakes, tsunamis, and other natural disasters; dynamics of turbulent flows and the motion of granular materials; the structure of atoms as expressed in the Standard Model and the formulation of the Standard Model and gravity into a Unified Theory; the structure of water; control of global infectious diseases; and also evolution and quantification of (ultimately) human cooperative behavior in politics, economics, business systems,

and social interactions. In fact, most of these issues have identified nonlinearities and are beginning to be addressed with nonlinear techniques, e.g., human longevity limits, the Standard Model, climate change, earthquake prediction, workings of the earth's interior, natural disaster prediction, etc.

The individual complex systems mathematical and modeling tools and scientific and engineering applications that comprised the *Encyclopedia of Complexity and Systems Science* are being completely updated and the majority will be published as individual books edited by experts in each field who are eminent university faculty members.

The topics are as follows:

Agent Based Modeling and Simulation
 Applications of Physics and Mathematics to Social Science
 Cellular Automata, Mathematical Basis of
 Chaos and Complexity in Astrophysics
 Climate Modeling, Global Warming, and Weather Prediction
 Complex Networks and Graph Theory
 Complexity and Nonlinearity in Autonomous Robotics
 Complexity in Computational Chemistry
 Complexity in Earthquakes, Tsunamis, and Volcanoes, and Forecasting and
 Early Warning of Their Hazards
 Computational and Theoretical Nanoscience
 Control and Dynamical Systems
 Data Mining and Knowledge Discovery
 Ecological Complexity
 Ergodic Theory
 Finance and Econometrics
 Fractals and Multifractals
 Game Theory
 Granular Computing
 Intelligent Systems
 Nonlinear Ordinary Differential Equations and Dynamical Systems
 Nonlinear Partial Differential Equations
 Percolation
 Perturbation Theory
 Probability and Statistics in Complex Systems
 Quantum Information Science
 Social Network Analysis
 Soft Computing
 Solitons
 Statistical and Nonlinear Physics
 Synergetics
 System Dynamics
 Systems Biology

Each entry in each of the Series books was selected and peer reviews organized by one of our university-based book Editors with advice and consultation provided by our eminent Board Members and the Editor-in-Chief.

This level of coordination assures that the reader can have a level of confidence in the relevance and accuracy of the information far exceeding than that generally found on the World Wide Web. Accessibility is also a priority and for this reason each entry includes a glossary of important terms and a concise definition of the subject. In addition, we are pleased that the mathematical portions of our Encyclopedia have been selected by Math Reviews for indexing in MathSciNet. Also, ACM, the world's largest educational and scientific computing society, recognized our *Computational Complexity: Theory, Techniques, and Applications* book, which contains content taken exclusively from the *Encyclopedia of Complexity and Systems Science*, with an award as one of the notable Computer Science publications. Clearly, we have achieved prominence at a level beyond our expectations, but consistent with the high quality of the content!

Palm Desert, CA, USA
August 2021

Robert A. Meyers
Editor-in-Chief

Volume Preface

Percolation concepts and ideas are appealing, partly for their simplicity and elegance, and partly for their wide applicability. Three decades ago, a colleague who himself was active in percolation-related research declared that “percolation as a research field is finished.” He was wrong! Development of percolation and its applications is not only continuing, but also thriving. In addition to its well-known applications, such as two-phase flow in porous media and conductivity of conducting-insulating composites, percolation has been used to explain phase transitions in many other systems in which connectivity of microscopic elements and their accessibility play fundamental roles in their macroscopic properties, including many in geography, epidemiology, the glass transition, speciation, heredity, sea ice prevalence, biological materials, spread of technology, and even boiling an egg, as well as the stock market. Many other applications are left out here and many more likely remain to be discovered. The deep relationships between percolation theory and disordered media help explain both its relevance and a lack of attention to the subject in traditional physics curricula. For, although the vast majority of Earth systems and materials are strongly disordered, the study of physics is still focused mainly on ordered, or nearly ordered, materials.

It is for such reasons that percolation and its applications represent an important subset of the study of complexity, though complexity is often considered to encompass chiefly such subjects as non-linear dynamics and chaos, or rule-based physics, and correlated or non-equilibrium systems. Indeed, in some professional societies, such as the American Geophysical Union, percolation as a subject is almost unknown and is not even a part of the curriculum of most of the participating institutions or fields, even though the relevance of percolation to characterization of rock, and in particular its fracture and fault network, and the spatial distribution of earthquake hypocenters was established several decades ago. But the fact remains that the importance of percolation theory spans across science.

The present collection, written by well-known experts of various applications of percolation theory, was originally a part of Springer’s online Encyclopedia of Complexity, which had been edited by one of us (M.S.). It was then decided that the collection should be turned into a book, as it covers a wide variety of subjects with one common theme, namely ideas and concepts of percolation theory. Thus, the authors of the original chapters were asked to update their parts, most of whom did. New chapters with emphasis on the most

recent applications were also solicited and received. The result is the present book. The fact is that there are so many distinct applications of percolation theory that it is practically impossible to cover them all in one volume and, therefore, many of the older and better-known applications were left out.

Some of the chapters address fundamental concepts in percolation theory, such as determination of the percolation threshold, both numerically and, if possible, their exact values, and the scaling theory of percolation clusters, perhaps the most important aspect of the theory, as well as segue to its applications. Others describe several variants of percolation, including bootstrap, invasion, continuum, correlated, and explosive percolation, which have expanded the scope of the potential applications. The remainder collectively describe various applications of percolation theory to novel problems with considerable relevance to societal issues of great importance, such as connections over networks, with relevance to threats and resilience; geochemistry, with relevance to the carbon cycle and climate change; fracture networks and porous media, important for water resources and exploration geophysics; and disordered materials, such as polymers, with a wide range of applications in manufacturing. We hope that our compilation will stir further interest in addressing additional problems, as well as generate greater recognition for the need to incorporate this particular manifestation of mathematical methods in the science curriculum, from the social to the natural.

We are grateful to all the contributors for agreeing to contribute a chapter in their field of expertise. We also thank our own past students and collaborators who helped us gain better understanding of percolation and advance its applications. Finally, we express our gratitude to Springer's staff for the Encyclopedia of Complexity for not only agreeing to turn the online collection into a book, but also helping us with all aspects of this task.

Los Angeles, California
Dayton, Ohio
August 2021

Muhammad Sahimi
Allen G. Hunt
Volume Editors

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About the Editor-in-Chief



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Biography

Dr. Meyers was manager of Energy and Environmental Projects at TRW (now Northrop Grumman) in Redondo Beach, CA, and is now president of RAMTECH Limited. He is coinventor of the Gravimelt process for desulfurization and demineralization of coal for air pollution and water pollution control and was manager of the Department of Energy project leading to the construction and successful operation of a first-of-a-kind Gravimelt Process Integrated Test Plant. Dr. Meyers is the inventor of and was project manager for the DOE-sponsored Magnetohydrodynamics Seed Regeneration Project which has resulted in the construction and successful operation of a pilot plant for production of potassium formate, a chemical utilized for plasma electricity generation and air pollution control. He also managed TRW efforts in magnetohydrodynamics electricity generating combustor and plasma channel development. Dr. Meyers managed the pilot-scale DoE project for determining the hydrodynamics of synthetic fuels. He is a coinventor of several thermo-oxidative stable polymers which have achieved commercial success as the

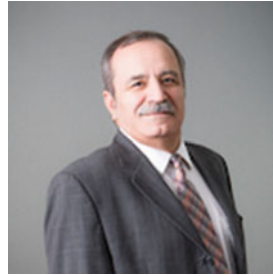
GE PEI, Upjohn Polyimides, and Rhone-Poulenc bismaleimide resins. He has also managed projects for photochemistry, chemical lasers, flue gas scrubbing, oil shale analysis and refining, petroleum analysis and refining, global change measurement from space satellites, analysis and mitigation (carbon dioxide and ozone), hydrometallurgical refining, soil and hazardous waste remediation, novel polymers synthesis, modeling of the economics of space transportation systems, space rigidizable structures, and chemiluminescence-based devices.

He is a senior member of the American Institute of Chemical Engineers, member of the American Physical Society, and member of the American Chemical Society and has served on the UCLA Chemistry Department Advisory Board. He was a member of the joint USA-Russia working group on air pollution control and the EPA-sponsored Waste Reduction Institute for Scientists and Engineers.

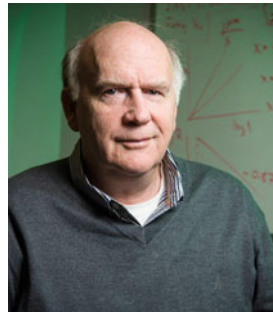
Dr. Meyers has more than 20 patents and 50 technical papers in the fields of photochemistry, pollution control, inorganic reactions, organic reactions, luminescence phenomena, and polymers. He has published in primary literature journals including *Science* and the *Journal of the American Chemical Society*, and is listed in *Who's Who in America* and *Who's Who in the World*. Dr. Meyers' scientific achievements have been reviewed in feature articles in the popular press in publications such as *The New York Times Science Supplement* and *The Wall Street Journal* as well as more specialized publications such as *Chemical Engineering* and *Coal Age*. A public service film was produced by the Environmental Protection Agency on Dr. Meyers' chemical desulfurization invention for air pollution control.

Dr. Meyers is the author or editor-in-chief of a wide range of technical books including the *Handbook of Chemical Production Processes*; the *Handbook of Synfuels Technology*; the *Handbook of Petroleum Refining Processes*, now in fourth edition; the *Handbook of Petrochemical Production Processes* (McGraw-Hill), now in a second edition; the *Handbook of Energy Technology and Economics*, published by John Wiley & Sons; *Coal Structure*, published by Academic Press; and *Coal Desulfurization* as well as the *Coal Handbook* published by Marcel Dekker. He served as chairman of the advisory board for *A Guide to Nuclear Power Technology*, published by John Wiley & Sons, which won the Association of American Publishers Award as the best book in technology and engineering. He also served as editor-in-chief of three editions of the Elsevier *Encyclopedia of Physical Science and Technology*. Most recently, Dr. Meyers serves as editor-in-chief of the *Encyclopedia of Analytical Chemistry* as well as *Reviews in Cell Biology and Molecular Medicine* and a book series of the same name both published by John Wiley & Sons. In addition, Dr. Meyers currently serves as editor-in-chief of two Springer Nature book series, *Encyclopedia of Complexity and Systems Science* and *Encyclopedia of Sustainability Science and Technology*.

About the Volume Editors



Muhammad Sahimi is professor of chemical engineering and materials science, and the NIOC chair in petroleum engineering at the University of Southern California in Los Angeles. He has been involved for over 40 years in the development of the applications of percolation theory to various fields, particularly in porous media, and heterogeneous materials.



Allen G. Hunt is appointed jointly in Physics and the Earth & Environmental Sciences Departments at Wright State University. He is author or editor of 5 books with 200 publications. His interests are currently in problems of environmental science with strong physics component, typically referenced to transport in disordered systems as addressed in percolation theory. An example is the ability to forecast the fate of precipitation falling on the continents, whether evapotranspiration or run-off (called the water balance). His teaching has been recognized by the Latter-Day Saints Student Association while teaching in a community college and, at Wright State, by election to Who's Who Among American Teachers.

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Percolation Phase Transition

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Article Outline

Glossary

Motivation and Definition

Introduction: Nature Is Disordered

What Is Percolation?

The Percolation Phase Transition

Percolation Properties

Universal Power Laws for the Percolation

Properties

Variants of Percolation Processes and Their

Applications

Future Directions

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Glossary

Accessible bonds or sites The retained bonds or sites in a percolation lattice that are connected to infinity via at least one path.

Backbone The set of (retained) bonds or sites in the sample-spanning percolation cluster that are connected to infinity by more than one independent path.

Bond percolation In a bond percolation model, a random lattice is formed from an infinite lattice by retaining each bond of the infinite lattice with probability p and deleting the rest. When a bond is retained, so also are its two ends sites.

Cluster A connected set of bonds or sites that are retained in a percolation lattice with probability p .

Correlation length The length scale below which a disordered percolation system cannot be regarded as homogeneous.

Critical exponents At the percolation thresholds, many percolation properties follow universal power laws, and the exponents that characterize such power laws are called *critical exponents*.

Percolation transition The connectivity or geometrical transition between a system in which a sample-spanning cluster of retained sites (or bonds) exists and one in which no such cluster exists.

Site percolation In a site percolation problem, a random lattice is formed from an infinite lattice by retaining each site of the infinite lattice with probability p and deleting the rest. A bond connecting two retained neighboring sites is also retained.

Motivation and Definition

This chapter describes the basic percolation problem. We begin by noting that most systems of scientific and practical applications are, at least at some scale, disordered. In a disordered medium, the connectivity of the elementary or microscopic elements has a profound effect on its macroscopic properties. The percolation transition occurs at the percolation threshold, which is the point at which the microscopic elements become connected for the first time and form a sample-spanning path or cluster across the medium. Percolation theory aims to describe the effect of the connectivity of the microscopic elements on the effective macroscopic properties of disordered media, particularly in the vicinity of the percolation threshold.

Introduction: Nature Is Disordered

It is well known that *Nature is disordered*. Pure, perfectly characterized, and geometrically immaculate systems are nowhere to be found, except perhaps in books and papers on theoretical phys-

ics. Although the concept of an infinite, perfectly periodic crystal lattice is incredibly elegant, it is as remote from experimental reality as possible. Even the best experimentalist who focuses on the purest of substances, such as carefully grown crystals, can hardly ever escape the effect of defects, trace impurities, and finite boundaries. Thus, we must come to terms with *disordered morphology*: variations in the shape and constitution that are often so ill-characterized that we must deem them to be random if we are to describe them or have any hope of doing so. The morphology of a medium has two major aspects: the *topology* – the interconnectiveness of its individual microscopic elements – and the geometry – the shapes and sizes of the individual elements.

At the same time, we believe, at least above the quantum mechanical level, in the doctrine of determinism, yet important *continua* exist in which deterministic descriptions of many phenomena are beyond hope. A well-known example is diffusion in which, at least over certain length scales, one observes an apparent random process – or *disordered dynamics*. The two types of disorder – morphological and dynamical – are often coupled and present simultaneously. An important example is fluid flow through a porous medium, where the interplay between the disordered morphology of the pore space and the dynamics of fluid motion gives rise to a rich variety of phenomena (Sahimi 1993, 2011).

Research on understanding the macroscopic properties of materials did make remarkable progress by using statistical mechanics and taking advantage of periodic structures and through the application of such equations as the Boltzmann's equation. Due to the rather obvious randomness in Nature, however, and because in the final analysis one always must confront the real disordered world, it became apparent in the 1960s that a statistical physics of disordered media must be developed to provide methods for deriving macroscopic properties of such media from the laws governing the microscopic world or, alternatively, for deducing their microscopic properties from the macroscopic observations and experimental data. Such a statistical physics of disordered media must take into account the effect of *both* the

topology and geometry of the media. Although the role of the geometry was appreciated as early as the beginning of the twentieth century, the effect of the topology was ignored for many decades or was treated in an ad-hoc manner, simply because it was thought to be too difficult to be taken into account rigorously.

History of science indicates that progress in any research field is not usually made with a constant rate, but rather in a sporadic manner. There are periods when a problem looks so difficult that we do not even know where or how to start analyzing it and periods when some seminal discoveries remove a great obstacle to progress and, thus, enable us to make a great leap forward. An excellent example is the discovery of a new class of superconducting materials by Bednorz and Müller (1986), who showed that it is possible to have superconductivity in certain Cu alloys at temperatures $T > 30$ K. Since their discovery (which brought them the Physics Nobel Prize in 1989), the field of superconductivity has advanced remarkably (after not making much progress for decades), so much so that we now have materials that can be superconducting at temperature well above 150 K.

Over the past four decades, the statistical physics of disordered media has been in a rapidly progressing phase, the reason for which is fourfold:

- (i) Rigorous theoretical methods for calculating the macroscopic (average) properties of disordered media have been developed.
- (ii) A large amount of accurate experimental data have been accumulated, thanks to many novel experimental techniques and instruments.
- (iii) Advances in computer technology and computational strategies have enabled us to use efficient numerical simulations for obtaining accurate estimates of many properties of disordered materials.
- (iv) The fourth, and perhaps the most important, reason for the rapid development of the statistical physics of disordered media is that, the effect of the interconnectivity of the microscopic elements of disordered media on their macroscopic properties has been

understood and appreciated. This has become possible through the development and application of percolation theory, the subject of this book.

What Is Percolation?

Consider electrical conduction through a composite material, a mixture of conducting, and insulating constituents or phases. Assume also that the two phases are randomly distributed. As an idealization, we represent the composite material by a simple cubic network in which each bond is either conducting with a finite conductivity or insulating with zero conductivity. Suppose also that we impose a voltage difference between two opposite faces of the network. The question that we ask is: What is the minimum fraction of conducting bonds for the formation of a sample-spanning cluster of such bonds, in order for the electrical current to flow through the material? This is clearly an important problem, because its solution tells us, for example, what (volume) fraction of a composite material, such as carbon black composites that are routinely used in many applications, must be conducting in order for the composite as a whole to be conducting.

Consider a second example. Imagine that the bonds of a simple cubic network represent the pore throats of a porous medium, for example, an oil reservoir. The pore throats are the narrow passages that connect the pore bodies. Most of the porosity of a porous medium (the void volume fraction in the porous medium) resides in the pore bodies. For brevity, we refer to the pore throats as pores. In reality, no porous medium looks as ordered as a simple cubic network, but as an idealization the model is useful. Now, suppose that the pores (bonds) are filled with oil, and that there are two wells in the system, one at A on one face, and a second one at B on the opposite face of the network. We try to push the oil out of the network (porous medium) by injecting water into the medium at A – the injection well – to produce oil at B – the production well. Oil and water do not mix with each other and, therefore, we assume that each pore is filled with either oil or

water. We also assume that water wets the surface of the pores (the wetting fluid), whereas oil does not (the nonwetting fluid). In many oil reservoirs, such as carbonate reservoirs of the Middle East, the opposite is true, but this does not make any difference to our discussion.

When the water is injected and pushed into the reservoir, it tries, due to being the wetting fluid, to find the *smallest pores* that it can reach and expel the oil from it. In reality, the process is more complex than what we are describing, but we ignore all the complications. The displaced oil is produced at well B. The question that we ask is: What fraction of the pores are filled with water when it reaches the production well at B *for the first time* (this is called the *breakthrough point*)? In other words, we would like to know what fraction of the pores lose their oil and, thus, how much oil is produced at well B at the breakthrough point. This is clearly an important question, given that the price of oil is now around \$75/barrel.

The Percolation Phase Transition

In the example of composite materials described above, if too many bonds (or too much of the materials) are insulating, no macroscopic current will flow through the materials, whereas for sufficiently large number of conducting bonds electrical current does flow in the materials, so that their macroscopic effective conductivity is nonzero. Assume that the fraction of the conducting bonds is p . Therefore, there must be a minimum or critical value p_{cb} of p , such that for $p \leq p_{cb}$ no electrical current would flow through the material and, therefore, the materials as a whole are insulating, whereas for $p > p_{cb}$ the materials become conducting.

In the example of displacement of oil by water, p represents the fraction of pores from which oil has been expelled and replaced by water. Therefore, for $p \leq p_{cb}$, water flows only locally and has not reached the production wall, whereas for $p > p_{cb}$ water flows between the injection and production wells. Thus, at any given time, p represents the fraction of the total oil in the

reservoir that has been recovered, while p_{cb} represents its value at the breakthrough point.

Therefore, it should be clear that, in both examples, p_c signifies a phase transition: for $p \leq p_{cb}$, there is no sample-spanning path of conducting bonds or pores filled by water, so that the system is macroscopically disconnected or *closed* to electrical current or flow of water. But, for $p > p_{cb}$ the system becomes macroscopically connected. Hence, p_{cb} is the point at which a *geometrical* phase transition from a disconnected to a connected system takes place. Percolation theory, then, quantifies the effect of the interconnectivity of the microscopic elements of a disordered medium (the conducting elements or the pores filled with water) on its macroscopic properties. p_{cb} is called the *bond percolation threshold* of the network.

We may also formulate the percolation problem in another way. Recall that most of the porosity of a porous medium resides in its pore bodies that connect the pore throats, as several pore throats meet at one pore body. Thus, in the pore network model of a porous medium described earlier, the nodes or sites of the network, which connect the pore throats or bonds, are the equivalent of the pore bodies. Then, in the example of the displacement of oil by water in a porous medium, the injected water pushes the oil from the sites (into the bonds) toward the production well. Since most of the porosity (the void space available for the fluids) resides in the pore bodies, to obtain a more accurate estimate of the volume of the oil recovered, we ask the question: At the breakthrough point, what fraction of the network's sites (pore bodies) are filled with water? Denoting this fraction by p_{cs} , it should be clear that it is the analogue of p_{cb} . p_{cs} is called the *site percolation threshold* of the network. For all two- and three-dimensional (3D) lattices, $p_{cs} > p_{cb}$.

Determining the exact percolation thresholds of many 2D and all the 3D lattices remains an unsolved problem. The chapter ► “Exact Percolation Thresholds” by Wierman describes and discusses the existing exact results for the percolation thresholds. Ziff's chapter ► “Efficient Simulation of Percolation Lattices” describes highly efficient numerical methods for estimating the percolation threshold and many other properties of percolation lattices.

Percolation Properties

Some of the most important properties of percolation systems that describe their morphology are as follows. For simplicity, we use p_c to denote p_{cs} or p_{cb} .

- (i) The *percolation probability* $P_\infty(p)$ is the probability that, when the fraction of occupied (conducting) bonds is p , a given site belongs to the sample-spanning (infinite) cluster of occupied bonds.
- (ii) The *accessible fraction* $A(p)$ is that fraction of occupied bonds (or sites) that belong to the infinite cluster.
- (iii) The *backbone fraction* $B(p)$ is the fraction of occupied bonds in the infinite cluster that actually contributes to a transport process, such as conduction, since some of the bonds in the infinite cluster are dead-end and do not carry any current. Therefore, $A(p) \geq B(p)$.
- (iv) The *correlation length* $\xi(p)$ is the typical radius of percolation clusters for $p < p_c$, and the typical radius of the “holes” above p_c that are generated by the vacant bonds or sites. For $p > p_c$, ξ is the length scale over which the system is macroscopically homogeneous.
- (v) The *average number of clusters of size s* (per lattice site) $n_s(p)$ is an important quantity in many of the problems of interest here because it corresponds to, for example, the number of conducting or insulating islands of a given size in a conductor–insulator composite solid.
- (vi) The probability that two sites, one at the origin and another one at a distance $\mathbf{r}$, are both occupied and belong to the same cluster of occupied sites, is $p^2 P_2(\mathbf{r})$, where $P_2(\mathbf{r})$ is called the *pair-connectedness function*.
- (vii) The *mean cluster size* S (also called the *site-averaged cluster number*) is the average number of sites in the cluster that contains a randomly selected site, and is given by,

$$S = \frac{\sum_s s^2 n_s(p)}{\sum_s s n_s(p)}. \quad (1)$$

Essam (1972) showed that S and the pair-connectedness function $P_2(\mathbf{r})$ are related through a simple relation:

$$S = 1 + p \sum_{\mathbf{r}} P_2(\mathbf{r}). \quad (2)$$

- (viii) Because a major application of percolation theory is the modeling of transport in disordered materials, and in particular composite solids, we must also consider the effective transport properties of percolation systems, namely their conductivity, diffusivity, elastic moduli, and dielectric constant. We first consider the conductivity of a two-phase composite material modeled as a two-component network in which each (randomly selected) bond has a conductance g_1 with probability p or g_2 with probability $q = 1 - p$. It is straightforward to show that the effective electrical (or thermal) conductivity σ_{eff} of the network is a *homogeneous function* and takes on the following form,

$$\sigma_{\text{eff}}(p, g_1, g_2) = g_1 F(p, h), \quad (3)$$

where $h = g_2/g_1$. Due to the assumption of randomness of the material's morphology, σ_{eff} is invariant under the interchange of g_1 and g_2 (phase-inversion symmetry) and we must, therefore, have

$$\begin{aligned} \sigma_{\text{eff}}(p, g_1, g_2) &= \sigma_{\text{eff}}(q, g_2, g_1), \text{ and } F(p, h) \\ &= hF(q, 1/h). \end{aligned} \quad (4)$$

The limit in which $g_2 = 0$ and g_1 is finite corresponds to a conductor–insulator mixture, already described above. In this case, as $p \rightarrow p_c$, more and more bonds are insulating, the conduction paths become very tortuous and, therefore, σ_{eff} decreases; at p_c one has $\sigma_{\text{eff}}(p_c) = 0$, since no sample-spanning conduction path exists any more. More generally, the conductance g_1 may follow a certain statistical distribution, which is in fact the case in most systems of practical importance, such as porous materials and composite solids.

The limit in which $g_1 = \infty$ and g_2 is finite represents a *conductor–superconductor*

mixture. All quantum mechanical aspects of real superconductors are ignored in this definition, and we are concerned only with the effect of the local connectivity of the material on the macroscopic conductivity. It is clear that the effective conductivity σ_{eff} of this system is dominated by the superconducting bonds. If $p < p_c$, then a sample-spanning cluster of the superconducting bonds does not exist and σ_{eff} is finite. As $p \rightarrow p_c^-$, σ_{eff} increases until a sample-spanning cluster of the superconducting bonds is formed for the first time at $p = p_c$, where σ_{eff} *diverges*. Note that both limits (g_1 finite and $g_2 = 0$, and $g_1 = \infty$ and g_2 finite) correspond to $h = 0$. Therefore, the point $h = 0$ at $p = p_c$ is particularly important. The chapter ► [“Conduction and Diffusion in Percolating Systems”](#) by Hughes elaborates on these aspects, and provides a full account of the state-of-the-art of this problem.

- (ix) In a similar manner, the elastic moduli of a two-phase composite solid, modeled by a percolation network, are defined. Consider a two-component network in which each bond is an elastic element (a spring or beam) which has an elastic constant e_1 with probability p or e_2 with probability $q = 1 - p$. The limit in which $e_2 = 0$ and e_1 is finite corresponds to composites of rigid materials and holes (e.g., porous solids). In such networks, as $p \rightarrow p_c$, more bonds have no rigidity, the paths for transmission of stress or elastic forces become very tortuous and, therefore, the effective elastic moduli E (Young's, bulk, or shear moduli) decrease; at p_c one has $E(p_c) = 0$. In general, the elastic constant e_1 can be selected from a statistical distribution.

The limit in which $e_1 = \infty$ and e_2 is finite represents mixtures of rigid–super-rigid materials. In this case the effective elastic moduli E of the mixture are dominated by the superrigid bonds. If $p < p_c$, then a sample-spanning cluster of the super-rigid bonds cannot form, and E is finite. As $p \rightarrow p_c^-$, the effective elastic moduli

increase until the percolation threshold p_c of the rigid phase is reached at which a sample-spanning cluster of the superrigid bonds is formed for the first time, and the effective elastic moduli *diverge*. The chapter ► “[Elastic Percolation Networks](#)” by Duxbury provides a comprehensive discussion of this subject.

- (x) The effective dielectric constant ϵ of a two-phase insulating composite material, modeled by a percolation network, may also be defined and, in fact, ϵ is closely related to the conductor–superconductor model described above (see, for example, Sahimi (2003)).
- (xi) Finally, the effective diffusivity D of a porous material is defined in a similar manner; see the chapter ► “[Conduction and Diffusion in Percolating Systems](#)” by Hughes.

Universal Power Laws for the Percolation Properties

One of the most important characteristics of percolation systems is their *universal* properties. The behavior of percolation quantities near p_c is insensitive to the microstructure (e.g., the coordination number) of the network and to whether the percolation process is a site or a bond problem. They follow *power laws* near p_c , characterized by *critical exponents* that are *universal*, as they depend only on the Euclidean dimensionality d of the system. We first describe the universal properties of the quantities that characterize the morphology of percolation systems and then present and discuss those of transport properties.

In general, the following power laws hold near p_c ,

$$P_\infty(p) \sim (p - p_c)^\beta, \quad (5)$$

$$A(p) \sim (p - p_c)^\beta, \quad (6)$$

$$B(p) \sim (p - p_c)^{\beta_b}, \quad (7)$$

$$\xi(p) \sim |p - p_c|^{-\nu}, \quad (8)$$

$$\zeta(p) \sim |p - p_c|^{-\gamma}, \quad (9)$$

$$P_2(\mathbf{r}) \sim \begin{cases} r^{2-d-\eta}, & p = p_c, \\ \exp(-r/\xi), & \text{otherwise,} \end{cases} \quad (10)$$

where $r = |\mathbf{r}|$. For large clusters near p_c , the cluster size distribution $n_s(p)$ is described by the following scaling law,

$$n_s \sim s^{-\tau} f[(p - p_c)s^\sigma], \quad (11)$$

where τ and σ are two more universal critical exponents and $f(x)$ is a scaling function such that $f(0)$ is not singular. The chapter ► “[Scaling Theory of Percolation Clusters](#)” by Stauffer and Sahimi elaborates further on these.

Similar power laws are also followed by the transport properties of percolation composites. In particular,

$$\sigma_{\text{eff}}(p) \sim (p - p_c)^t, \text{ conductor} \\ \text{— insulator composites} \quad (12)$$

$$\sigma_{\text{eff}}(p) \sim (p_c - p)^{-s}, \text{ conductor} \\ \text{— superconductor composites} \quad (13)$$

$$E(p) \sim (p - p_c)^T, \text{ rigid — soft composites} \quad (14)$$

$$E(p) \sim (p_c - p)^{-S}, \text{ rigid} \\ \text{— superrigid composites.} \quad (15)$$

For length scales $L < \xi$, the resistance R between two end points of a box of linear size L scales with L as $R \sim L^\zeta$. It is not difficult to show that

$$t = (d - 2)\nu + \zeta, \quad (16)$$

where, $\zeta = \zeta_r$. It has been shown (Straley 1977) that in 2D, $t = s$.

The power law that characterizes the behavior of the effective diffusivity $D(p)$ near p_c is derived from that of $\sigma_{\text{eff}}(p)$, and is shown to be given by

$$D(p) \sim (p - p_c)^{t-\beta}. \quad (17)$$

The implied prefactors in all the above power laws depend on the type of lattice and are *not* universal.

Equations (12) and (13) can be unified by using the two-component resistor network described above. In the critical region, that is, the region near p_c , where both $|p - p_c|$ and $h = g_2/g_1$ are small, the effective conductivity σ_{eff} follows the following scaling law (Efros and Shklovskii 1976; Straley 1976)

$$\sigma_{\text{eff}} \sim g_1 |p - p_c|^t \Phi_{\pm}(h|p - p_c|^{-t-s}). \quad (18)$$

where Φ_+ and Φ_- are two homogeneous functions corresponding, respectively, to the regions above and below p_c , and are, similar to t and s , universal. For any fixed and nonzero h , σ_{eff} has a smooth dependence on $p - p_c$. This becomes clearer if we rewrite Eq. (18) as

$$\sigma_{\text{eff}} \sim g_1 h^{t/(t+s)} \Psi \left[|p - p_c| h^{-1/(t+s)} \right], \quad (19)$$

where $\Psi(x) = x^t \Phi_+(x^{-t-s}) = (-x)^t \Phi_-[(-x)^{-t-s}]$. Since the function $\Psi(x)$ is universal, the implication of Eq. (19) is that, if one plots $\sigma_{\text{eff}}/[g_1 h^{t/(t+s)}]$ versus $|p - p_c| h^{-1/(t+s)}$ for all networks (or randomly disordered materials) that have the same Euclidean dimensionality, all the results (or measurements) should collapse onto a single universal curve. This provides a powerful tool for estimating the conductivity of a composite for any value of h , given the conductivities for two other values of h (by which the universal curve is constructed). Somewhat similar, but more complex, scaling equations can be developed for the elastic moduli, dielectric constant, and other properties of percolation composites.

No exact relation is known between the transport and morphological exponents. This is because the transport exponents describe *dynamical* properties of disordered materials and media, whereas the morphological exponents characterize their *static* properties. In general, there is no reason to expect a direct relation between the two.

If two physical phenomena in heterogeneous media that contain percolation-type disorder are

described by two different sets of critical exponents, then the physical laws governing the two phenomena must be fundamentally different. Thus, critical exponents help one to distinguish between different classes of problems and the physical laws that govern them. Moreover, since the numerical values of the percolation properties are not universal and vary from one system to another, but the scaling and power laws that they follow near p_c are universal and do not depend on the details of the system, estimates of the critical exponents for a certain phenomenon are used for establishing the relevance of a particular percolation model to that phenomenon in disordered materials.

Variants of Percolation Processes and Their Applications

Let us now describe some well-established applications are described. It should be clear that a percolation network is created when sites or bonds are blocked or removed and, therefore, the macroscopic connectivity of the system is gradually reduced. In the example of the composite materials, the bonds or sites are blocked to the conduction. In the example of displacement of oil by water in a porous medium, the bonds or sites are blocked to oil (since it is expelled from such sites or bonds). Therefore, percolation networks are also useful as simple models of any disordered medium in which the connectivity of the medium's microscopic elements influences its macroscopic properties. Moreover, the main concepts of percolation theory are simple and, therefore, writing computer program for simulating a percolation process is conceptually straightforward, if we do not wish to simulate very large networks. Thus, percolation networks may also serve as a simple tool for introducing students to computer simulation of disordered media. Stauffer and Aharony (1994) and Hughes (1996) emphasize the theoretical foundations of percolation theory, while Sahimi (1994, 2003, 2011) describes its important applications.

Although percolation in regular lattices – those in which the coordination number Z , the number

of bonds connected to the same site, is the same everywhere – has been extensively invoked for studying the morphology and transport properties of many disordered materials, percolation in continua and in topologically random networks – those in which the coordination number varies from site to site – are also of great interest, since in many practical situations one may encounter such irregular and continuous media. For example, continuum percolation is directly applicable to characterization and modeling of the morphology and effective transport properties of micro-emulsions, polymer blends, sintered materials, sol-gel transitions, and many more.

In the percolation phenomena described so far, no correlations between various segments of the system (e.g., bonds and/or sites, or their transport properties) were assumed. However, disorder in many important heterogeneous materials is not completely random. There usually are correlations of some extent that may be finite but large. For example, in packing of solid particles, there are short-range correlations, whereas large-scale porous media contain long-range correlations. The universal scaling properties of percolation systems with finite-range correlations are the same as those of random percolation, if the length scale of interest is larger than the correlation length. Moreover, if the correlation function $C(r)$ decays as r^{-d} or faster, where d is the Euclidean dimensionality of the system, then the scaling properties of the system are identical with those of random percolation. This is not totally unexpected because even in random percolation, as p decreases toward p_c , correlations begin to build up and, therefore, the introduction of any type of correlations with a range shorter than the percolation correlation length ξ cannot change its scaling properties. In many other cases, for example, large-scale porous media and some disordered elastic materials, there are long-range correlations.

A particular type of percolation model with extended correlations is known as the *bootstrap percolation*. In this problem sites of a lattice are initially randomly occupied. Then, those sites that do not have at least Z_c nearest-neighbor occupied sites are removed (note that $Z_c = 0$ is the usual

random percolation). The interactions between the sites are short-ranged, but the correlations between them may build up as the distance between two occupied sites also increases. The original motivation for developing this model was to explain the behavior of some disordered materials in which magnetic impurities are randomly distributed in a host of non-magnetic metals. It is believed that in some of such materials an impurity atom cannot sustain a localized magnetic moment unless it is surrounded by a minimum number of magnetic neighbors. Bootstrap percolation has proven to be a complex problem with a rich variety of unusual properties that are a strong function of the parameter Z_c . For example, an important question is the nature of the percolation transition in this model. It now appears that for sufficiently high values of $Z_c \leq Z$ (where Z is the coordination number of the lattice), the percolation transition is *first order*, that is, discontinuous, whereas for low values of Z_c the transition is continuous and second order. If the phase transition is of first-order type, then the percolation threshold of the system is, in fact, $p_c = 1$, the sample-spanning cluster is compact, and power laws (5), (6), (7), (8), (9), (10), (11), (12), (13), (14), and (15) are no longer valid.

An important application of percolation theory has been description of two-phase fluid flow in porous media, a simple example of which was described earlier. Since one fluid is injected into a porous medium – that is, it invades the medium – in order to displace a second fluid, this particular model is usually known as the *invasion percolation* (IP), which is different from random percolation, because in the IP bonds or sites are not removed at random but according to the principle of least resistance path. In addition, percolation provides a powerful tool for modeling of the effect of the connectivity of fractures and faults on fluid flow and transport properties of rock, a highly complex set of phenomena.

Significant advances have been made to generalize the standard percolation model. In particular, one such generalization has been utilized to model network glasses and proteins, for which the question of macroscopic rigidity and the conditions under which it exists is paramount.

Another important and well-established application of percolation is to modeling of the rheology of polymers and gels, particularly in the vicinity of the gelation point. Several variants of the percolation models have been developed in order to address this important problem.

Percolation has been used to describe the topography of Earth and Mars, an interesting and unusual application. In addition, percolation has been fruitfully utilized to quantitatively describe water partitioning in soil.

A more recent application of percolation has been to problems in complex networks, particularly scale-free networks. The concepts of percolation have been used to study not only the robustness and vulnerability of random networks, but also addressing such important problems as immunization and epidemic spreading in populations and computer networks, communication paths, and fragmentation in social networks.

A new form of percolation is called explosive percolation (EP), which is a general phenomenon that often results as a consequence of delaying the emergence of large-scale connectivity in a random network or lattice system. While the usual percolation phase transition describes the onset of large-scale connectivity among the nodes of a network or sites on a lattice as the density of connections increases, in the EP one begins from a completely disconnected system and adds connections at random following some prescribed algorithm that repeatedly suppresses the onset of large-scale connectivity. In processes that display the EP, the onset can be significantly delayed but, once the percolation transition is inevitably reached, large-scale connectivity emerges drastically, exhibiting a substantial discontinuous jump in any finite system. For some phenomena exhibiting the EP, the transition is extremely abrupt yet ultimately continuous in the thermodynamic limit. The scaling properties in the critical regime are, however, distinct from any previously known universality class. Other algorithms exhibiting EP can be shown to be truly discontinuous transitions, due to the underlying mechanisms, such as growth by overtaking, correlated percolation, cooperative percolation, and evolution on hierarchical lattices.

Future Directions

Theoretically, most aspects of percolation are well understood. Exact values of most of the critical exponents (in 2D), or their very accurate numerical estimates (in 3D), are known. Exact values of the bond and site percolation thresholds of several 2D lattices are also known, as are very accurate numerical estimates of the percolation thresholds of many 3D lattices, although we still do not know the exact value of, for example, the site percolation threshold of the square lattice. Thus, theoretically, the grand challenge is to develop general methods for obtaining the exact percolation thresholds of 3D lattices and the exact values of the critical exponents for 3D systems, although the latter challenge may well be beyond reach.

Therefore, aside from the theoretical challenges described above, most of the future work on percolation will be concentrated on its applications to problems of practical importance, examples of which are described in this book.

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Introduction to Percolation

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Why is percolation theory relevant to the analysis of complex systems? The question can be answered only if we first define a complex system. I spent a large amount of time in vain, searching for a “clean,” generally accepted definition of a complex system, until I finally realized that there are probably as many definitions as the number of scientists that deal with complex systems – there is not a clean *universal* definition of a complex system.

But, at the very least, we can agree that a complex system consists of a large number of interacting components, or parts. The interactions may be short- or long-ranged, and may or may not change with time. One type of such interactions is the *connectivity*, the way the components or parts of a complex system are connected with each other. Clearly, if the components or parts of a complex system are not connected, they do not interact with each other, at least not directly. Now, if the connectivity of the components or parts of a complex system plays an important role on the macroscopic, or effective, properties of the system, then, percolation theory plays a prominent – and in fact a decisive – role in quantifying the effect of the connectivity on the effective properties of that complex system.

Percolation processes are, in fact, the *opposite* of diffusion processes. In the latter case, the diffusant decides where to diffuse or move. The medium in which the diffusant is moving does not have any influence on the motion. This explains why many diffusion processes can be reduced to problems in essentially one-dimensional systems, because all that matters is the distance r of the diffusant from the origin of its motion, which are, therefore, amenable to rigorous theoretical analysis and analytical solutions.

In a percolation process, on the other hand, it is the medium that decides where a species can go. Therefore, if the connectivity of the components or different parts of the medium – the complex system – is poor, the species cannot go far. If, on the other hand, the parts are well-connected, then the species is free to go almost anywhere. In political jargon, a complex system in which the connectivity of its different parts or components plays a decisive role in determining its effective properties – i.e., a percolation system – is like a corrupt society in which what matters is the connectivity to the powerful people! If one is well-connected, one can advance rapidly; if not, there is little prospect for advancement. Since most systems of practical interest are three- or at least two-dimensional, percolation problems are far more difficult to solve than the diffusion problem.

Why should the connectivity of a complex system be poor? Because natural complex systems are *disordered*. In fact, Nature, the most complex system that we know of, is disordered. Pure and geometrically perfect (periodic) systems are nowhere to be found, except perhaps in books and in our imaginations. One way that the disorder manifests itself is in the connectivity of the parts or components of a complex system. In some sectors of the system the parts are well connected, while in other sectors they are not. But what matters most is the *overall* connectivity of the system, so that a given phenomenon can take place *across* the system.

An illuminating example is provided by porous materials. A piece of rock is a disordered porous medium: The shapes, sizes, and orientations of the pores are not identical, but vary greatly. If we attempt to characterize their statistical distributions, we find them to be broad. Thus, such porous media are highly disordered and complex. Clearly, the way the pores are connected plays a crucial role in flow of a fluid through the medium, which is why percolation is relevant to the description of fluid flow in disordered porous medium.

But, many of the man-made systems are also disordered, and the connectivity of their parts is a controlling factor in determining their effective

properties. For example, small molecules, or monomers, react, form chemical (covalent) bonds between themselves, and create a macromolecule. The structure of such a macromolecule is highly disordered. Clearly, the effective properties of the macromolecule are controlled by the connectivity of the monomers or the small molecules that formed it. If each monomer reacts with only two other monomers, it has a connectivity of two. The macromolecule has, therefore, no branches or loops. If, on the other hand, each monomer reacts with several others and has a higher connectivity, one obtains branched polymers and gels, the properties of which are completely different from those of linear polymers.

As another example, consider electrical conduction through a composite material, a mixture of conducting and insulating phases. Assume that the conducting and insulating phases are randomly distributed in the composite. For simplicity, we model the composite material by a simple-cubic network in which each bond is either conducting with a finite conductivity, or insulating with zero conductivity. Suppose that we impose a voltage difference between two opposite faces of the network. The question, then, is: what is the minimum fraction of the bonds with a finite conductivity in order for the electrical current to flow through the material, so that it is macroscopically conducting? This is clearly an important practical question, because its answer tells us, for example, what (volume) fraction of carbon black composites that are used in many applications must be conducting in order for the composites as a whole to be conducting.

If too many bonds are insulating, no macroscopic current will flow through the material, whereas for sufficiently large number of conducting bonds electrical current does flow in the material, so that its macroscopic effective conductivity is nonzero. If the fraction of the conducting bonds is p , then, there must be a minimum or critical value p_c of p , such that for $p \leq p_c$ no electrical current would flow through the material and, therefore, the material as a whole is insulating, whereas for $p > p_c$ the material becomes conducting.

The quantity p_c signals a phase transition: for $p \leq p_c$ there is no sample-spanning path of conducting bonds, so that the material is

macroscopically insulating. For $p > p_c$, on the other hand, the system becomes macroscopically conducting – the conducting bonds form a sample-spanning conducting cluster. Hence, p_c is the point at which a *geometrical* phase transition from a disconnected to a connected system takes place. Percolation theory, then, quantifies the phase transition and its effect on the macroscopic properties of a complex system. p_c is called the *percolation threshold* of the medium.

Determination of the exact percolation thresholds of many 2D and all the 3D lattices remains an unsolved problem. Wierman's chapter ▶ [“Exact Percolation Thresholds”](#) describes and discusses the existing exact results for the percolation thresholds. Ziff's chapter ▶ [“Efficient Simulation of Percolation Lattices”](#) describes highly efficient numerical methods for estimating the percolation threshold and many other properties of percolation lattices, while the chapter ▶ [“Scaling Theory of Percolation Clusters”](#) by Dietrich Stauffer and the author describes the theoretical foundations for many important percolation properties near the percolation threshold.

Although percolation in regular lattices – those in which the coordination number Z , the number of bonds connected to the same site, is the same everywhere – has been extensively invoked for studying the morphology and transport properties of many disordered materials, percolation in continua and in topologically random networks – those in which the coordination number varies from site to site – are also of great interest, since in many practical situations one may encounter such irregular and continuous media. For example, continuum percolation is directly applicable to characterization and modelling of the morphology and effective transport properties of micro-emulsions, polymer blends, sintered materials, sol-gel transitions, and many more. The chapter ▶ [“Principles of the Theory of Continuum Percolation”](#) by Balberg describes the advances that have been made in understanding of the percolation effects in continuous systems, and in random networks.

In the percolation phenomena described so far, no correlations between various segments of the system (for example, bonds and/or sites, or their

transport properties) were assumed. However, disorder in many important heterogeneous materials is not completely random. There usually are correlations of some extent that may be finite but large. For example, in packing of solid particles, there are short-range correlations, whereas large-scale porous media contain long-range correlations. The universal scaling properties of percolation systems with finite-range correlations are the same as those of random percolation, if the length scale of interest is larger than the correlation length. Moreover, if the correlation function $C(r)$ decays as r^{-d} or faster, where d is the Euclidean dimensionality of the system, then the scaling properties of the system are identical with those of random percolation. This is not totally unexpected because even in random percolation, as p decreases toward p_c , correlations begin to build up and, therefore, the introduction of any type of correlations with a range shorter than the percolation correlation length ξ cannot change its scaling properties. In many other cases, e.g., large-scale porous media and some disordered elastic materials, there are long-range correlations. The chapter ▶ [“Correlated Percolation”](#) by Coniglio and Annalisa Fierro describes the major differences between percolation in random and correlated systems.

A particular type of percolation model with extended correlations is known as the *bootstrap percolation*. In this problem, sites of a lattice are initially randomly occupied. Then, those sites that do not have at least Z_c nearest-neighbor occupied sites are removed (note that $Z_c = 0$ is the usual random percolation). The interactions between the sites are short-ranged, but the correlations between them may build up as the distance between two occupied sites also increases. The original motivation for developing this model was to explain the behavior of some disordered materials in which magnetic impurities are randomly distributed in a host of nonmagnetic metals. It is believed that in some of such materials an impurity atom cannot sustain a localized magnetic moment unless it is surrounded by a minimum number of magnetic neighbors. Bootstrap percolation has proven to be a complex problem with a rich variety of unusual properties that are a strong function of the

parameter Z_c . For example, an important question is the nature of the percolation transition in this model. It now appears that for sufficiently high values of $Z_c \leq Z$ (where Z is the coordination number of the lattice), the percolation transition is *first order*, i.e., discontinuous, whereas for low values of Z_c , the transition is continuous and second order. If the phase transition is of first-order type, then the percolation threshold of the system is, in fact, $p_c = 1$, the sample-spanning cluster is compact, and power laws (5)–(15) are no longer valid. The chapter ▶ [“Bootstrap Percolation”](#) by De Gregorio et al. describes this important area of percolation problems.

The chapter ▶ [“Invasion Percolation”](#) by Knackstedt and Paterson describes in detail application of the percolation model to two-phase fluid flow in porous media, a simple example of which was already described above. Since, as described above, one fluid is injected into a porous medium – that is, it invades the medium – in order to displace the second fluid, this particular model is usually known as the *invasion percolation*. Other aspects of the application of percolation in problems on fluid flow through porous media are described in the chapter ▶ [“Percolation in Porous Media”](#) by King and Masihi.

Percolation also provides a powerful tool for modeling of the effect of the connectivity of fractures and faults on fluid flow and transport properties of rock, a highly complex set of phenomena. Thus, in their chapter ▶ [“Percolation, Faults and Fractures in Rock,”](#) Adler et al. describe the recent application of percolation to this important problem.

The chapter ▶ [“Conduction and Diffusion in Percolating Systems”](#) by Barry Hughes provides a detailed description of diffusion and conduction in disordered and composite materials, including porous media, and presents a comprehensive account of the state of the art of this important application of percolation to a problem of great practical importance.

Deformation and stress transport in disordered materials are important to a wide variety of phenomena in science and technology, ranging from elastic properties of solid materials to viscoelastic properties of polymers and gels, and rigidity of

biological materials (cells, proteins, bones, etc.). The application of percolation to modeling of such phenomena has proven to be highly successful and fruitful. The chapter ► [“Elastic Percolation Networks”](#) by Duxbury provides a comprehensive discussion of the subject, and describes the theoretical foundations and computer simulation methods for stress transport in disordered percolation systems.

Two other chapters expand on what Duxbury describes in his chapter. Thorpe describes recent advances on generalization of the percolation model, and its application to modeling of proteins and other biological materials. The question of the rigidity of such materials is addressed. An important and well-established application of percolation is to modeling of the rheology of polymers and gels, particularly in the vicinity of the gelation point. Several variants of the percolation models have been developed in order to address this important problem. The chapter ► [“Percolation Phase Transition”](#) by Sahimi describes the advances that have been made in this area.

Percolation has been used to describe the topography of Earth and Mars. The chapter ► [“Application of Percolation Theory to Statistical Topographies”](#) by Saberi describes this interesting and unusual application. In addition, percolation has been fruitfully utilized to quantitatively describe water precipitation in soil; see the chapter ► [“Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock”](#) by Hunt and coworkers.

The chapter ► [“Percolation in Complex Networks”](#) by Cohen and Havlin describes application of percolation to problems in complex networks, particularly scale-free networks. They show how the concepts of percolation are used to study not only the robustness and vulnerability of

random networks but also such problems as immunization and epidemic spreading in populations and computer networks, communication paths, and fragmentation in social networks.

A new form of percolation is called explosive percolation (EP), which is a general phenomenon that often results as a consequence of delaying the emergence of large-scale connectivity in a random network or lattice system. While the usual percolation phase transition describes the onset of large-scale connectivity among the nodes of a network or sites on a lattice as the density of connections increases, in the EP one begins from a completely disconnected system and adds connections at random following some prescribed algorithm that repeatedly suppresses the onset of large-scale connectivity. In processes that display the EP, the onset can be significantly delayed but, once the percolation transition is inevitably reached, large-scale connectivity emerges drastically, exhibiting a substantial discontinuous jump in any finite system. For some phenomena exhibiting the EP, the transition is extremely abrupt yet ultimately continuous in the thermodynamic limit. The scaling properties in the critical regime are, however, distinct from any previously known universality class. Other algorithms exhibiting EP can be shown to be truly discontinuous transitions, due to the underlying mechanisms, such as growth by overtaking, correlated percolation, cooperative percolation, and evolution on hierarchical lattices. The chapter ► [“Explosive Percolation Processes”](#) by D’Souza provides an excellent introduction to the subject.

We would like to thank all the authors that agreed to contribute a chapter to this book. It takes considerable time and efforts to put together reviews that describe the most important aspects of a given phenomenon, and the progress that has been made in studying it.

Exact Percolation Thresholds

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Article Outline

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Glossary

Archimedean lattices A *regular tiling* is a tiling of the plane which consists entirely of regular polygons. (A regular polygon is one in which all side lengths are equal and all interior angles are equal.) An *Archimedean lattice* is the graph of vertices and edges of a regular tiling which is vertex-transitive, i.e., for every pair of vertices, u and v , there is a graph isomorphism that maps u to v . There are exactly 11 Archimedean lattices. A notation for Archimedean lattices, which can also serve as a prescription for constructing them, is given in Grünbaum and Shephard (1987). Around any vertex (since all are equivalent, by vertex-transitivity), starting with the smallest polygon touching the vertex, list the number of edges of the successive polygons around the vertex. For convenience, an exponent is used to indicate that a number of successive polygons have the same size.

Bond percolation In a bond percolation model, a random subgraph is formed from an infinite graph G by retaining each edge of G with probability p , independently of all other edges.

Dual graph A graph is planar if it may be drawn in the plane with no edges intersecting except at their endpoints, thus dividing the plane into faces. Every planar graph G has a dual graph, denoted here by $D(G)$. $D(G)$ may be constructed by placing a vertex of $D(G)$ in each face of G and connecting two vertices of $D(G)$ by an edge if the corresponding faces in G share a common edge. Note that $D(D(G)) = G$.

Line graph The line graph, $L(G)$, of a graph G is constructed by placing a vertex of $L(G)$ on each edge of G and connecting two vertices of $L(G)$ if the corresponding edges of G share a common endpoint.

Matching graphs A pair of matching graphs may be constructed from an underlying planar graph. Select a set F of faces of the graph. Construct a graph G by adding an edge in each face of F between any pair of vertices that are not already connected by an edge. Construct the matching graph $M(G)$ of G by adding an edge between any pair of vertices in each face not in F that are not already connected by an edge. Note that $M(M(G)) = G$.

Percolation threshold In a percolation model with parameter p , there is a retention probability p_c , called the percolation threshold, above which the random subgraph contains an infinite connected component and below which all connected components are finite.

Periodic graph A periodic graph is an infinite graph that can be represented in d -dimensional space so that it is invariant under translations by all integer linear combinations of a fixed basis.

Site percolation In a site percolation model, a random graph is formed from an infinite graph G by retaining each vertex of G with probability p , independently of all other vertices. An edge of G is retained in the random graph if both its endpoint vertices are retained.

Definition of the Subject

Percolation models were introduced in the 1950s by Broadbent and Hammersley (1957) to model the flow of fluid in a random medium. Since both terms, fluid and medium, may be broadly interpreted, percolation has a wide variety of applications, including thermal phase transitions, oil flow in sandstone, and the spread of epidemics. An important motivation for the development of percolation models was to provide an alternative to diffusion models, in which the randomness was associated with the fluid while the medium is relatively homogeneous. Since percolation models associate the randomness with the medium, it is possible for the fluid either to become trapped or to flow infinitely far. This presence of a phase transition is an important reason for the importance of percolation models. The percolation threshold is a critical probability in the percolation model which corresponds to the phase transition point. Since the emphasis in percolation theory is on the effect of the medium on the behavior of the model, it is important to understand how the percolation threshold depends on the characteristics of the medium.

The medium is often, but not always, modeled by a periodic graph, representing an atomic lattice structure. In the bond percolation model, each edge of the graph is retained with probability p , independently of all other edges, to create a random subgraph. In the site percolation model, each vertex of the graph is retained with probability p , independently of all other vertices, and each edge is retained if and only if both its endpoints are retained. In both models, the focus is on the properties – in particular, the size – of the connected components, called clusters, of the random subgraph.

The most common definition is that the percolation threshold is a retention probability value p_c such that if $p > p_c$ there exists an infinite cluster in the graph and if $p < p_c$ there are only finite clusters in the graph. However, there exist other interpretations, which correspond to different definitions of the percolation threshold: (1) A percolation threshold p_H is the critical probability above which a specific vertex v is in an infinite cluster

with positive probability. The percolation threshold p_H is independent of the specific vertex v if the graph is connected. (2) A percolation threshold p_T is defined as the critical probability above which the expected cluster size containing a specific vertex v is infinite, and is also independent of the choice of v if the graph is connected. (3) For periodic graphs, a percolation threshold p_S may be defined in terms of the limiting behavior of the probability that a cluster connects opposite sides of a rectangle in a sequence of similar rectangles whose areas are increasing to infinity. For the periodic graphs discussed in this article, these definitions provide equal values for the percolation threshold.

Due to the dependence of the percolation threshold on the features of the lattice, since the origins of percolation theory much research has been devoted to deriving exact values, computing simulation estimates, and proposing approximation formulas for the percolation threshold as a function of the lattice. This article focuses on the extent of knowledge of exact values of percolation thresholds for bond percolation and site percolation on various graphs.

Introduction

Although the percolation threshold problem is simply described and easily visualized, it has become recognized as extremely intractable, with the result that, after 50 years of research, exact percolation thresholds are known for few graphs. Besides the trivial one-dimensional case, and infinite regular trees, the only solutions are for two-dimensional graphs. There are no exact solutions for periodic graphs in three dimensions or higher.

We now provide a brief history of the development of exact percolation thresholds and the mathematical tools used.

The first major development was in 1960 by Harris (1960), who proved a lower bound of $1/2$ for the square lattice bond model threshold. The value was larger than simulation estimates at that time, and was believed to be sharp. Harris used the self-duality of the square lattice extensively in the

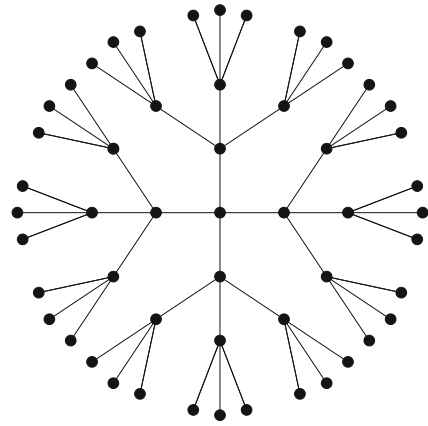
proof, and established a lemma regarding covariant events which was later generalized by Fortuin et al. (1971) and played a crucial role in later exact percolation threshold proofs.

Recognizing the importance of duality in the study of bond percolation, Sykes and Essam (1964) developed a corresponding concept of matching graphs for site percolation models. Interpreting the percolation threshold as a singularity of a clusters-per-site function, they derived values of the bond percolation thresholds for the square, triangular, and hexagonal lattices. Their methods implied that site percolation thresholds of matching graphs sum to one, and bond percolation thresholds of dual graphs sum to one. A key transformation in the solutions for the triangular and hexagonal lattices was a star-triangle transformation relating the two graphs. However, their exact values would not be given mathematically rigorous proofs until much later.

Although they did not establish the exact percolation thresholds, Seymour and Welsh (1978), in the context of the square lattice bond model, laid important groundwork for the solution that followed. They recognized and defined the p_H , p_T , and p_S interpretations of the percolation threshold, and proved relationships among them. Russo (1978, 1981) independently established similar results for the square lattice site model.

In 1980, Kesten (1980) rigorously established that the percolation threshold of the square lattice bond model is $1/2$, using the self-duality of the square lattice, and proving that all versions of the percolation threshold are equal in this case (Figs. 1 and 2).

Using Kesten's methods, the duality of the triangular and hexagonal lattices, and the star-triangle transformation between them, in 1981 Wierman (1981) proved that the bond percolation threshold of the triangular lattice is the root of $1 - 3p + p^3$ in the interval $[0, 1]$, which is equal to $2 \sin(\pi/18) \approx 0.347296$, and the bond percolation threshold of the hexagonal lattice is the complementary value, approximately 0.652704 . In 1984, Wierman (1984b) discovered another pair of dual lattices for which the exact bond percolation threshold could be determined using a version of the star-triangle transformation. The bond



Exact Percolation Thresholds, Fig. 1 A portion of a Cayley tree with vertex degree four

threshold of the bowtie lattice is the root of the polynomial $1 - p - 6p^2 + 6p^3 - p^5$ in $[0, 1]$, which is approximately 0.404518 , while the bond threshold of its dual graph is the complementary value, approximately 0.595482 .

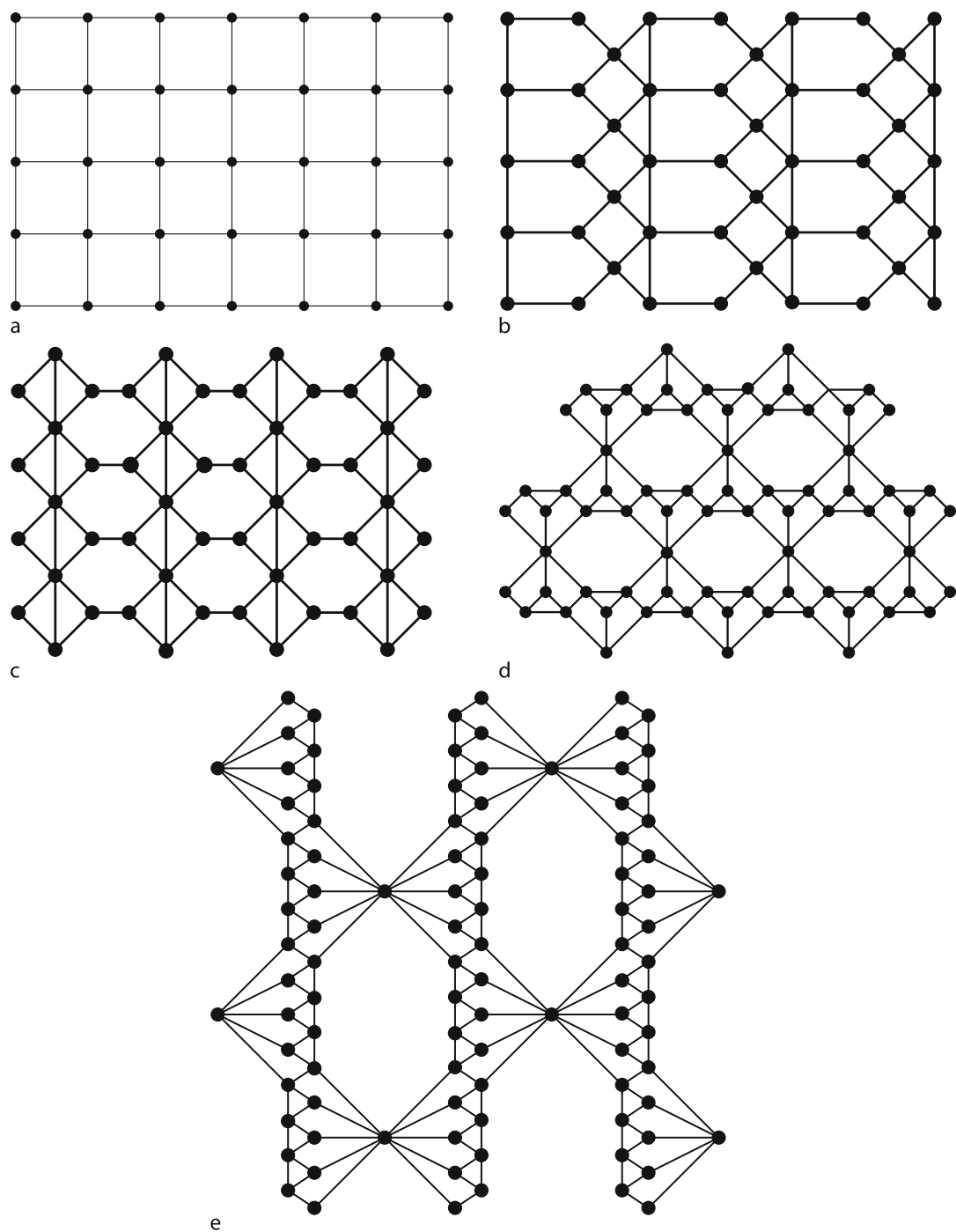
These results were generalized by Kesten (1982) in his 1982 monograph, where he proved that the site percolation thresholds of a pair of periodic matching graphs sum to one. Since it is fully-triangulated and therefore self-matching, the triangular lattice has percolation threshold equal to one-half. The duality result for bond percolation thresholds is implied by this result via the bond-to-site transformation (Figs. 3 and 4).

In 2006, Scullard (2006), Ziff (2006), Ziff and Scullard (2006) derived exact bond percolation thresholds of additional periodic lattices based on the star-triangle transformation.

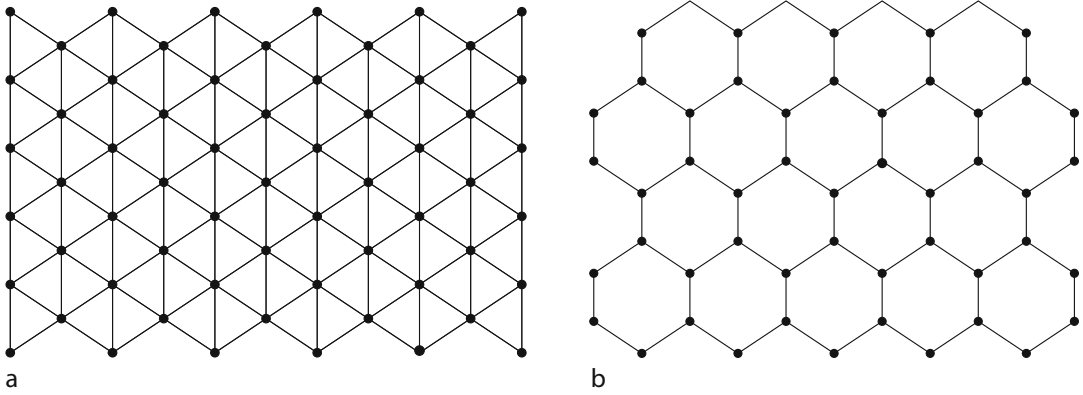
Exact percolation thresholds can be derived for additional graphs that are obtained by various transformations of graphs with exact solutions. Such solutions can be established via the bond-to-site transformation, subdivision of edges, and replacing edges with more complex decorations.

Trees

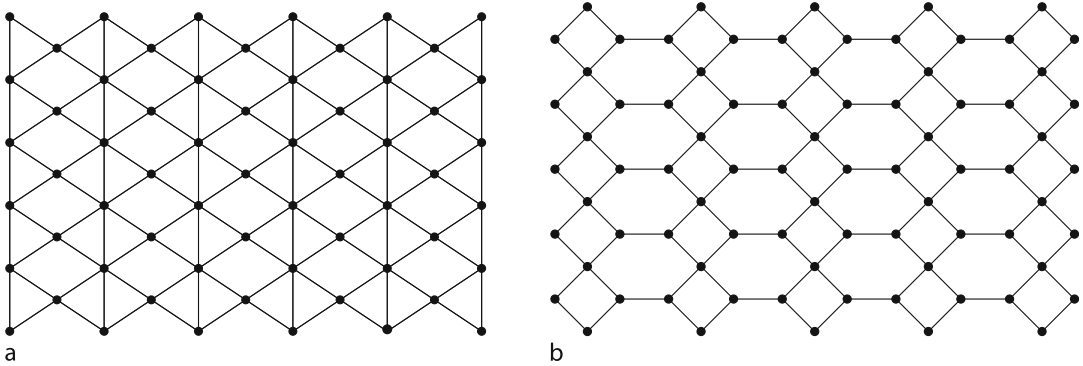
A tree is a graph which is connected and has no cycles, or equivalently, which has a unique path between every pair of vertices. An infinite tree in



Exact Percolation Thresholds, Fig. 2 Portions of five self-dual periodic graphs. The square lattice is at the *upper left*. An example of the generalization to a family of self-dual graphs is at the *bottom*



Exact Percolation Thresholds, Fig. 3 Portions of the triangular (a) and hexagonal or honeycomb (b) lattices



Exact Percolation Thresholds, Fig. 4 Portions of the bow-tie lattice (a) and its dual lattice (b)

which every vertex has the same degree is called a Cayley tree or Bethe lattice.

The earliest non-trivial exact percolation threshold solutions were for Cayley trees. Let C_k denote the Cayley tree of degree k . Then, for all $k \geq 3$,

$$p_c(C_k) = \frac{1}{k-1},$$

for both bond percolation and site percolation.

It is easy to see that the bond and site percolation thresholds are equal. In a bond model on a Cayley tree, consider starting from a specific vertex, called the root, and moving outward. For each edge, consider the vertex at the end farthest from the root to be retained or not according to whether the edge is retained or not.

This creates a site percolation model with the same parameter value as the original bond percolation model, in which there is an infinite cluster if and only if there is an infinite cluster in the bond model. Thus, the percolation thresholds of the two models are equal.

The values of the thresholds for Cayley trees can be determined either by calculation of the probability that a vertex is in an infinite component or by elementary theory of branching processes.

Lyons (1990) has shown that, for rooted trees in general, an average number of branches per vertex, called the branching number, may be defined. The percolation threshold of the tree is the reciprocal of the branching number. However, the definition of the branching number is rather intricate, so exact percolation thresholds are not easily computed.

Two-Dimensional Bond Models

Planarity plays an important role in establishing exact bond percolation thresholds in two-dimensional models. A graph is planar if it may be drawn in the plane with no edges intersecting except at their endpoints, thus dividing the plane into faces. Every planar graph G has a dual graph, denoted here by $D(G)$. $D(G)$ may be constructed by placing a vertex of $D(G)$ in each face of G and connecting two vertices of $D(G)$ by an edge if the corresponding faces in G share a common edge. Note that $D(D(G)) = G$.

The computational importance of dual graphs is that the bond percolation thresholds of a pair of periodic matching graphs sum to one, as implied via the bond-to-site transformation by a result of Kesten in 1982.

Without an additional relationship between the pair of dual graphs, duality itself does not yield an exact percolation threshold solution. However, if the two graphs are isomorphic, the common graph is said to be self-dual, and its bond threshold must be one-half. Thus, the bond percolation threshold of the square lattice is exactly one-half.

Besides the square lattice, there are other periodic self-dual graphs, which, for the same reason, have a bond percolation threshold equal to one-half. Figure 2 shows additional self-dual graphs, and illustrates a construction of an infinite family of periodic self-dual graphs, given in Wierman (2006).

Essentially all other exact bond threshold solutions are derived using a relationship called the star-triangle transformation, first used by Sykes and Essam. Notice that the set of edges of the triangular lattice may be decomposed into triangles that are similarly oriented. If each triangle is replaced by a three-pointed star with the points at the vertices of the triangle, the resulting graph is the hexagonal lattice, which is the dual graph of the triangular lattice. If retention probability parameters of the two lattices can be found so that the probabilities of all possible events involving connections of the three vertices on the boundary of the triangle are equal, then the exact percolation threshold can be

determined. The solution is the root of a polynomial involving the retention probability of the triangular lattice: $1 - 3p + p^3$, giving the solution $2 \sin(\pi/18) \approx 0.347296$. By duality, the bond threshold for the hexagonal lattice is $1 - 2 \sin(\pi/18) \approx 0.652704$. While this solution was derived by Sykes and Essam in 1964, mathematical methods to rigorously prove it were not developed until later, with the result being proved by Wierman in 1981.

Modified versions of the star-triangle transformation were used to derive other exact bond percolation thresholds. Wierman discovered a pair of lattices, called the bowtie lattice and its dual, which could be solved exactly. The bond threshold of the bow-tie lattice is the root of $1 - p - 6p^2 + 6p^3 - p^5$, which is approximately 0.404518, while the dual lattice has threshold approximately 0.595482.

Scullard (2006), Ziff (2006), Ziff and Scullard (2006) used a modified star-triangle approach to find values for a lattice that they named the martini lattice, and applied the approach to other planar two-dimensional graphs. They use a triangle-triangle transformation in the derivation of their results. While their approach does produce correct exact percolation threshold results for some graphs, further study is needed to determine the complete range of validity of their method.

For any of the exact bond threshold solutions, additional exact thresholds may be determined for certain transformations of the graphs.

If each edge of a graph G is replaced by k edges in series, the resulting graph is called a k -subdivision of G . Since the k edges in series play the role of one edge of G , the bond percolation threshold of a k -subdivision of G is the k th root of the bond threshold of G .

More generally, instead of replacing each edge by a series of edges, one may replace it by some finite graph connecting only the two endpoints, which is called a decoration by Ord and Whittington (1980). By calculating the edge retention probability that makes the probability of connection through the decoration equal to the threshold of the original graph, the percolation threshold of the decorated graph may be exactly determined.

Site Models in Two Dimensions

A key concept for the understanding of exact percolation threshold solutions for two-dimensional site models is the idea of a matching pair of graphs, introduced by Sykes and Essam in 1964.

A pair of matching graphs is constructed from an underlying planar graph. Select a set F of faces of the graph. Construct a graph G by adding an edge between any pair of vertices in each face of F that are not already connected by an edge. Construct the matching graph $M(G)$ of G by adding an edge between any pair of vertices in each face not in F that are not already connected by an edge. Note that $M(M(G)) = G$. Note also that if the underlying planar graph has faces with more than three sides, then at least one of the graphs in the matching pair is nonplanar (Figs. 5 and 6, Table 1).

The importance of matching graphs is that the site percolation thresholds of a pair of periodic matching graphs sum to one, as proved by Kesten (1982) in 1982. In fact, this result implied the result for bond percolation thresholds for dual graphs, via the bond-to-site transformation.

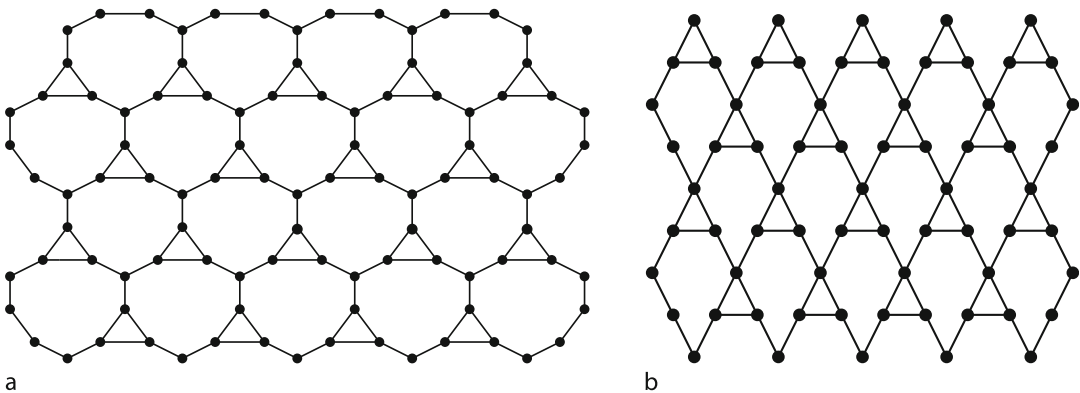
In general, additional information besides the matching property is needed to identify the exact percolation thresholds of the pair of graphs. However, if the matching graphs are identical, the graph is called self-matching, and the percolation threshold is necessarily one-half. Note that if a planar graph has all triangular faces, then it is

self-matching. Therefore, the site percolation threshold is exactly one-half for the triangular lattice and the dual graphs of the $(4, 8^2)$, $(4, 6, 12)$, and $(3, 12^2)$ lattices. In addition, there are self-matching graphs that are not fully-triangulated, such as the line graph of the square lattice, shown in Fig. 7.

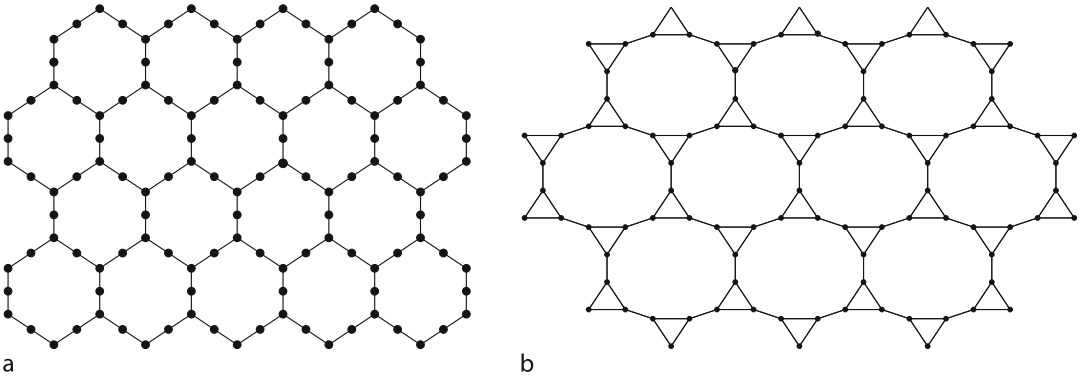
As a caution, however, note that a fully-triangulated graph may not have its site percolation threshold equal to one-half if it is not a periodic graph. An example of a fully-triangulated graph with site percolation threshold equal to one was given by van den Berg (1981), and further discussion of similar counterexamples is provided in Wierman (1984a) (Fig. 8).

Scullard (2006), Ziff (2006), Ziff and Scullard (2006) have also proposed exact site percolation thresholds for additional two-dimensional lattices.

Additional exact site percolation threshold solutions have been obtained by transformations of bond models with exact solutions. The line graph, $L(G)$, of a graph G is constructed by placing a vertex of $L(G)$ on each edge of G and connecting two vertices of $L(G)$ if the corresponding edges of G share a common endpoint. If there is a bond percolation model on G with each edge retained with probability p independently of the other edges, one may define a site percolation model on $L(G)$ in which each vertex is retained if and only if the corresponding edge of G is retained. Then, an infinite cluster in the bond model on G corresponds to an infinite cluster in the site



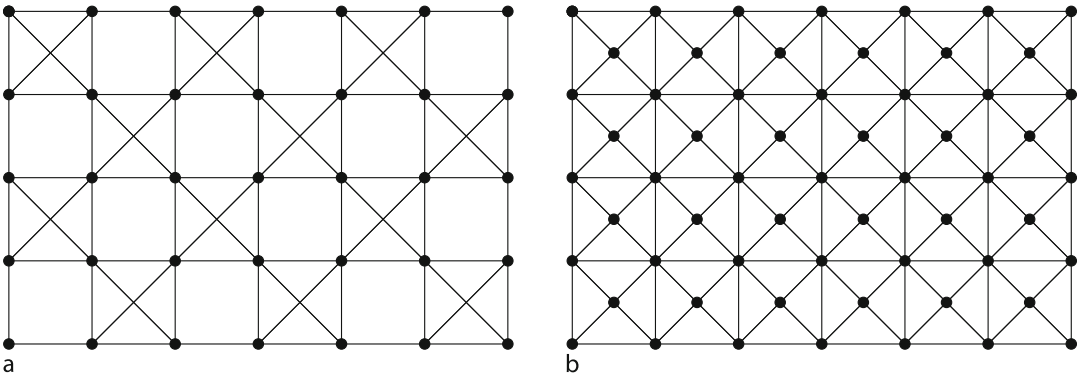
Exact Percolation Thresholds, Fig. 5 Portions of the martini lattice (a) and martini-A lattice (b)



Exact Percolation Thresholds, Fig. 6 Portions of the 2-subdivision of the hexagonal lattice (a) and its line graph, the $(3, 12^2)$ lattice (b)

Exact Percolation Thresholds, Table 1 Exact bond percolation thresholds of selected lattice graphs

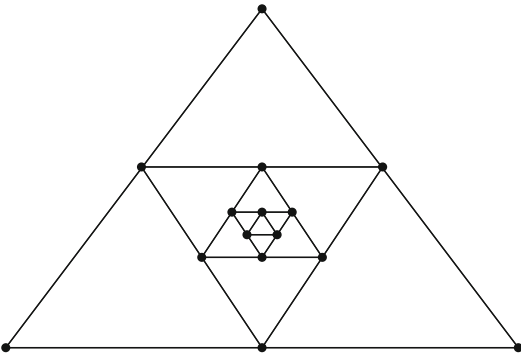
Lattice	Bond Threshold	Equation
Triangular = (3^6)	$2 \sin \pi/18 \approx 0.347296$	$p^3 - 3p + 1 = 0$
Bow-tie	0.414518	$1 - p - 6p^2 + 6p^3 - p^5 = 0$
Square = (4^4)	0.500000	$2p - 1 = 0$
Self-dual	0.500000	$2p - 1 = 0$
D(Bow-tie)	0.595482	$1 - p_c(\text{Bow-tie})$
Martini-A	0.625457	$p^5 - 4p^4 + 3p^3 + 2p^2 - 1 = 0$
Hexagonal = (6^3)	0.652704	$1 - p_c(3^6)$
Martini	$1/\sqrt{2} \approx 0.707107$	$(2p^2 - 1)(p^4 - 3p^3 + 2p^2 + 1) = 0$



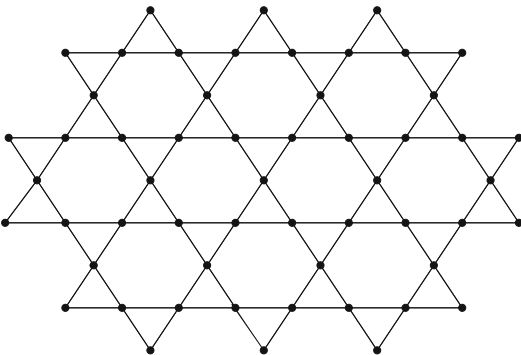
Exact Percolation Thresholds, Fig. 7 Two self-matching lattices: the line graph of the square lattice (a) and the dual of the $(4, 8^2)$ lattice (b)

model on $L(G)$, so the percolation thresholds of the two models are equal. This construction and relationship is called the bond-to-site transformation, and allows translation of all exact bond percolation threshold solutions into exact site percolation threshold solutions on line graphs.

For example, the line graph of the hexagonal lattice, called the Kagomé lattice, has a site percolation threshold of exactly $1 - 2 \sin(\pi/18) \approx 0.652704$, while its matching graph, the line graph of the triangular lattice, has exact site percolation threshold $2 \sin(\pi/18) \approx 0.347296$. As



Exact Percolation Thresholds, Fig. 8 A portion of van den Berg’s counterexample: The graph is fully-triangulated, and thus self-matching, but has percolation threshold equal to one – not one-half



Exact Percolation Thresholds, Fig. 9 A portion of the Kagomé lattice, which is the line graph of the hexagonal lattice

another example, the site percolation threshold of the $(3, 12^2)$ lattice is exactly $\sqrt{1 - 2 \sin(\pi/18)} \approx 0.807901$, since it is the line graph of the 2-subdivision of the hexagonal lattice (Fig. 9, Table 2).

Random Voronoi Percolation

In 2006, Bollobás and Riordan (2006a) provided the first exact percolation threshold solution for a continuum percolation model.

Consider the set of points P in a two-dimensional homogeneous Poisson point process. For a point $p \in P$, the Voronoi polygon of p is the set of all points in the plane that are closer to

Exact Percolation Thresholds, Table 2 Exact bond percolation thresholds of selected lattice graphs

Lattice	Site threshold	Equation
Triangular = (3^6)	0.500000	$2p - 1 = 0$
Self-matching	0.500000	$2p - 1 = 0$
Kagomé = $(3, 6, 3, 6)$	0.652704	$p = p_c(6^3\text{bond})$
$(3, 12^2)$	0.807901	$p = \sqrt{p_c(6^3\text{bond})}$

p than to any other point in P . Each Voronoi polygon is a convex polygon, and two Voronoi polygons either intersect in an edge or not at all. The edges of the collection of Voronoi polygons form an infinite planar graph called the Voronoi tessellation corresponding to P .

The dual of the Voronoi tessellation is called the Delaunay triangulation, since with probability one all faces are triangles. The remarkable result of Bollobás and Riordan (2006a) is that the site percolation threshold of the Delaunay triangulation is exactly one-half.

Multiparameter Critical Surfaces

For some applications, multi-parameter percolation models are considered. For example, in a bond percolation model, edges in different directions may have different retention probability parameters, giving a multi-dimensional parameter space. In such a parameter space, the role of the percolation threshold is played by the boundary between regions of the parameter space where infinite clusters occur and where all clusters are finite, called the critical surface.

Some multi-parameter bond percolation models are exactly solved. Two notable examples are: (1) In the square lattice with vertical edges retained with probability p and horizontal edges retained with probability q , the critical surface is the line segment $p + q = 1$. (2) For the triangular lattice with retention probabilities r, s , and t for bonds in the three different directions, the critical surface is the surface given by $1 - r - s - t + rst = 0$.

Future Directions

As seen above, the exact bond or site percolation threshold is known for relatively few lattices, with the exact solutions restricted to infinite trees and two-dimensional periodic graphs. Although they have been studied extensively, exact thresholds are not known for such common graphs as the square lattice site model, the hexagonal lattice site model, and the Kagomé lattice bond model. Although there are tools such as duality and matching, there is no general method available for providing exact threshold values. The grand challenge is to find the exact bond or site percolation threshold for a lattice in three dimensions or higher.

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Efficient Simulation of Percolation Lattices

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Article Outline

Glossary

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Glossary

Accessible hull The hull with pinched off “fjords” removed.

Hoshen–Kopelman algorithm A technique where a lattice (in 2d) is scanned one row at a time, and clusters are identified using information from the previous row only.

Hull The boundary of a percolation cluster, either internal or external.

Hull-generating walk A way to generate the hull of a percolation cluster by a type of kinetic self-avoiding walk.

Leath algorithm A technique where individual percolation clusters are “grown” from a seed by an epidemic type of process.

Newman–Ziff algorithm A way to efficiently generate microcanonical (fixed occupancy) states and from them to study all canonical (fixed p) states.

Queue A computer list construct in which the events are stored in such a way that the first in is the first out (also called “FIFO” or “breadth-first searching”).

Recursion A programming method in which a procedure calls itself, creating new local variables each time.

Stack A computer list construct in which the events are stored in such a way that the last in is the first out (also called “LIFO” or “depth-first searching”).

Stochastic Loewner evolution (SLE) A theoretical way to study conformally invariant random curves, including the hulls of percolation clusters, through a transformation of simple Brownian motion. Also called Schramm–Loewner Evolution.

Tree A data structure in which points are connected in a tree-like structure with branches but no loops.

Definition of the Subject

Percolation is a simple model of the formation of longrange connectivity in random systems. While it can be solved exactly in a few cases of branched lattices, and while many results in two dimensions (2d) can be found exactly, most of the work in this field is intimately connected with computer simulation. Various algorithms have been developed over the years, and this article surveys some of them, especially related to cluster sizes and connectivity, and the hull.

Introduction

Percolation was introduced by Flory in 1941 (Flory 1941) for branched networks (polymers) and Broadbent and Hammersley in 1957 for lattice networks, and its study by computer simulation began just a few years later (Vyssotsky et al. 1961). The overall development of the percolation

field in the ensuing years has been intimately connected with advances in simulation and computer algorithms. Specific computer algorithms allow optimal simulation of different aspects of the percolating system, and the results of these simulations have provided information and ideas for theoretical developments and further understanding of this fundamental problem. Recent advances have allowed, for some examples, the determination of numerical thresholds to very high precision, the demonstration (later confirmed by theory) that universality applies to crossing and excess cluster properties, and the universality of scaling functions and their resulting amplitude ratios.

The basic percolation system is a lattice with sites (vertices) and/or bonds (edges) occupied with a given probability p , and the computational problem is to identify and characterize the clusters of adjacently occupied sites (site percolation) or of sites connected by the bonds (bond percolation), and determine properties such as the size distribution, conductivity, and crossing. In principle, these are generally rather straightforward problems, but in practice, the challenge is to do things efficiently so that large systems can be simulated over many times to get high numerical significance.

In this article, we will describe and summarize several algorithms that have been developed to simulate percolation. Explicit fragments of programming in C are given. The emphasis of the article is on the computational methods, and we use some recent examples of application to illustrate them. We do not address the large number of advances that have been made recently in the percolation field mainly by mathematicians, based upon Stochastic Loewner Evolution (SLE) (Schramm 1999) and related methods. For a recent review, see (Gruzberg 2006).

Another area of recent interest related to percolation is in the study of networks, including Erdős–Renyi random graphs (1959), scale-free and small world networks. For these models, percolation corresponds to the formation of a “giant component”. Because of the lack of loops over large distances, the percolation

properties can generally be solved for analytically (i.e., Moore and Newman 2000; Rozenfeld and ben-Avraham 2007). Some of these results are closely related to percolation on the branch-free Bethe lattice, whose solution goes back to Flory and was analyzed in detail by Fisher and Essam (1961). However, in this review we will only consider regular lattices, and not the algorithms and results related to these systems.

Cluster Identification and Growth

Consider a lattice, say square for simplicity, and suppose that the sites have been “populated” by being made “occupied” (OCC) with probability p and empty or “vacant” (VAC) with probability $1 - p$. (Here we are considering site percolation.) A basic problem is to identify the clusters, and to determine some property such as the size distribution n_s (the number of clusters of size s , divided by the total number of sites on the lattice) or whether crossing exists between two intervals on the boundary. Here we describe two neighbor-search methods to identify clusters: the depth-first or last-in, first-out (LIFO) method using recursion, and the breadth-first or first-in, first-out (FIFO) method using a queue.

In the following programs, we use a simple two-dimensional array `lat[x][y]` to represent a rectangular $W \times H$ system with a square lattice. For many problems it is more efficient to use a one-dimensional array and add 1, -1 , W , and $-W$ for the four directions (in 2d, for example), using wrap-around at the end to form “helical” boundary conditions, which for a large system is practically equivalent to a periodic one. (The helicity adds a “twist” to the boundaries, which can have an effect on some of the properties when it is large enough (Ziff et al. 1999)). Later on, in section “The Microcanonical-Canonical Method”, we will give an example of a program which uses a one-dimensional array and also a neighbor array that can be used to program periodic boundary conditions precisely, with a bit more programming overhead however.

Recursive Search (LIFO)

In the recursive search method, the lattice (say of dimensions $W \times H$) is first scanned for new, unchecked sites:

```
for (xo = 0; xo < W; ++xo)
  for (yo = 0; yo < H; ++yo)
    if (lat[xo][yo] == OCC)
      { lat[xo][yo] = TAGGED;
        FindNeighbors(xo,yo); }
(P1)
```

where TAGGED means that the site has been checked and won't be checked again. Then the cluster belonging to that site is found using the FindNeighbors subroutine, which is given by

```
FindNeighbors(int x,y)
{ int dir;
  for (dir = 0; dir < 4; ++dir)
    { xp = x + dx[dir];
      yp = y + dy[dir];
      if (lat[xp][yp] == OCC)
        { lat[xp][yp] = TAGGED;
          FindNeighbors(xp,yp); } } }
(P2)
```

When an OCC neighbor is found for the first time, it is checked by calling the same routine over again. Here we used the four nearest-neighbor direction vectors $dx[0]=1$, $dy[0]=0$, $dx[1]=0$, $dy[1]=1$, $dx[2]=-1$, $dy[2]=0$, $dx[3]=0$, $dy[3]=-1$. We have not dealt with the boundaries in this example. Open boundaries can be simulated by adding a perimeter of VAC sites; periodic boundary conditions can be simulated simply by writing $lat[xp \& (W-1)][yp \& (H-1)]$ for $lat[xp][yp]$, where $\&$ is the bit-wise “and” operation, if W and H are exactly powers of two. As the clusters are identified, the number of occupied sites can be counted, moments determined, etc. Crossing can be determined if a single cluster touches two given boundaries. For periodic b.c., one typically considers not crossing but wraparound.

The above FindNeighbors program uses recursion and the compiler stores unchecked xp , yp and the local dir in the stack; recursion uses a “last in, first out” (LIFO) or “depth-first” (Tarjan

1972) method that can cause problems (exhaust the available stack memory) for very large clusters.

Making a Queue (FIFO)

A more memory-efficient method to search for neighbors is to use a “queue” where one keeps a list of unchecked sites, and visits them in a first-in, first-out (FIFO) fashion. However, one must construct the list explicitly; the recursive method won't do it. We need functions to put and remove coordinates from the queue; here we use %define statement functions (which creates in-line text) for efficiency:

```
%define PutOnQueue(X,Y) \
{ xlist[putindex] = X; \
  ylist[putindex] = Y; \
  ++putindex; }
(P3)
```

and

```
%define GetFromQueue(X,Y) \
{ X = xlist[getindex]; \
  Y = ylist[getindex]; \
  ++getindex; }
(P4)
```

where we start the simulation with $getindex = putindex = 0$. The way the above lists are written, they must be dimensioned to be as large as the largest possible cluster; however, by making the list size S exactly a power of two, the list can be shortened and “recycled” simply by writing $xlist[putindex \& (S-1)]$ etc. The size S has only to be as large as the number of growth sites of a cluster, which grows as roughly the square root of the maximum size of the cluster. For example, for a lattice of size 1024×1024 , it is more than sufficient to make $S = 4096$. To test for an error in the recycled queue, the line `if (putindex == getindex)...` can be added after `++putindex;` in (P3).

To make use of the queue, (P1) is kept the same except that the last line is replaced by `PutOnQueue(xo,yo)`, followed by the loop


```

do
{ GetFromQueue(x,y)
  for (dir = 0; dir < 4; ++dir)
  { xp = x + dx[dir];
    yp = y + dy[dir];
    if ((lat[xp][yp]) == OCC)
    { lat[xp][yp] = TAGGED;
      PutOnQueue(xp,yp); } }
} while (getindex != putindex);

```

(P5)

When the two indices `putindex` and `getindex` are equal to each other, there are no more occupied sites to check and the search is complete.

Note that the lists `xlist` and `ylist` can also be used for the LIFO method by treating them as a stack rather than a queue – that is, by using only one index and to decrement the index when a set of coordinates is taken off the stack. This is a way to program the LIFO method without using the recursive feature of the C language.

Generating Occupied Sites or Bonds as you go – the Leath Method

In the above algorithms, the sites or bonds were made occupied or vacant ahead of time. An alternative scheme is to start with all sites in an UNVISITED state, and make them OCC or VAC when they are first encountered. For example, in (P5), starting from the sixth line, we would write instead

```

if ((lat[xp][yp]) == UNVISITED)
  if (random() < probab)
  { lat[xp][yp] = OCC;
    PutOnQueue(xp,yp); }
else lat[xp][yp] = VAC;

```

(P6)

where `random()` is the random number generator and `probab` is the probability. Here, the label TAGGED is not needed, because a site is added to the queue as soon as it is made occupied. Before putting the first site `x0, y0` on the queue, one also has to call the random number generator to determine whether that site is occupied.

When this program is applied to the growth of a single cluster (that is, starting with just one `x0` and `y0`), it is commonly called the Leath method,

although it is not carried out in the same way as in Leath (1976), where larger diamond-shaped regions of the lattice around the cluster are successively probed. In fact, the idea of looking at clusters wetting a single site was carried out in the earliest simulations of percolation (Vyssotsky et al. 1961).

The above growth scheme works particularly nicely in the case of bond percolation, especially when the clusters are characterized solely by the sites they connect, and not by the number or arrangement of the bonds that connect them. In this case, (P6) is kept exactly the same except the last line “else lat[xp][yp] = VAC;” is removed. This is because one can consider bond percolation as a spreading or epidemic process (Grassberger 1983) from site to site along the occupied bonds; if a bond is not occupied, the fluid will not spread to the next site, but that does not preclude fluid from another cluster to visit that neighboring unvisited site. Sites with no bonds are considered to be clusters of size $s = 1$. Whether a bond is made occupied or not, that bond will never be considered again, so its state does not have to be remembered. Not all bonds of a cluster are generated in this method – for example, the fourth bond in a simple square arrangement will not be tested – but the four sites of the cluster will be sampled with the correct weight. In this process, one effectively generates a minimum spanning tree (with no loops) that connects every site on a cluster.

Note that this procedure checks (or grows) the cluster one growth shell at a time. Each growth shell is at a successive value of the minimum (Pike and Stanley 1981) or “chemical” (Havlin and Nossal 1984) distance from the seed, so this method is useful for studying minimum distance problems including the fractal dimension $d_{\min}$. Like d_B , its value is not known exactly even in 2d and has to be determined by simulation. In 2d, its value is $d_{\min} = 1.1307(4)$ (Grassberger 1992).

The Hoshen–Kopelman Algorithm

The Hoshen–Kopelman algorithm (Hoshen and Kopelman 1976) has been a mainstay of work on percolation and is fairly well-known. It is described in some detail in the article of

Stauffer in this work ► [Scaling Theory of Percolation Clusters](#) and so will just be described briefly here.

The main idea of this algorithm is that a percolating system (say in two dimensions) can be examined or created a row at a time, and the cluster statistics can be updated just from the knowledge of the connections in the previous row. In d -dimensions, one must remember the state of the previous surface in $(d - 1)$ -dimensions. The connections can be remembered in a look-up table, or a rooted-tree data structure can be used.

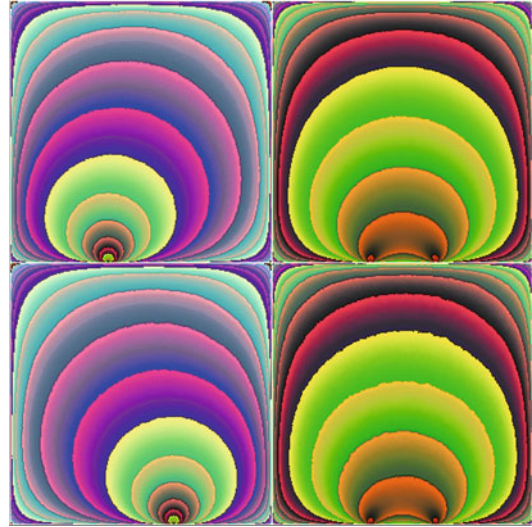
This algorithm can be used to analyze the clusters statistics of a given, fully populated system, or it can be used as a very memory efficient scheme (especially in 2d) to generate and analyze on the fly a large system, since only the previous row (in $2 - d$) needs to be remembered. Using this scheme, Tiggemann has simulated a lattice of $4,000,000^2$ sites (Tiggemann 2001).

To actually identify all of the clusters on a given lattice, it is faster to sweep across the lattice using one of the neighbor-search algorithms above, because in the HK method the lattice would have to be swept a second time in order to get the most updated cluster labels.

Recently, Deng and Blöte (2005) used a version of the Hoshen–Kopelman algorithm to determine $p_c = 0.5927465(4)$ for site percolation on the square lattice, and $p_c = 0.3116077(4)$ for site percolation on the simple cubic lattice, using a novel method of analysis based upon universal ratios of correlation functions and moment distributions. Tiggemann (2001) has used a massively parallel version to study percolation on lattices in two, three, and four dimensions. A good discussion the the HK algorithm, its antecedents in the computer science field, and some of its modifications and extensions, is given by Martín-Herrero (2004).

Example: Critical Density Plots

As an example of an application of the above simulation method, we show in Fig. 1 the average density of clusters anchored to a single point and simultaneously to two points at the boundary of a square system. Here the density is defined as the number of times a given site is



Efficient Simulation of Percolation Lattices, Fig. 1 Simulation results for the average density of clusters touching the left anchor (*top left*), right anchor (*bottom left*), both anchors simultaneously (*lower right*), and prediction from Eq. (2) (*upper right*). (From Kleban et al. (2006))

connected to the corresponding boundary point, divided by the total number of realizations. We use bond percolation with the growth algorithm and the FIFO (queue) method, with `xlist` and `ylist` large enough to remember the largest possible cluster. This allows us to transfer the coordinates of the cluster to the appropriate array (touching one anchor, touching the other anchor, or touching both anchors) after the cluster is grown. In this simulation, we don't have to scan the entire lattice, but just use the two anchor points as seeds (x_0, y_0) for the cluster growth/identification.

To analyze this problem theoretically, it is convenient to put the system on the complex plane, and consider a half-infinite system $y \geq 0$, with the boundary placed on the real axis, and anchors at x_a and x_b . The results of this calculation can be transformed to a square by a standard conformal map $w(z)$, using the transformation of the density $\rho(w) = (dw/dz)^{-h} (d\bar{w}/d\bar{z})^{-\bar{h}} \rho(z)$ where $h = \bar{h} = (2 - D)/2 = 5/96$ for $2 - d$ percolation, and D is the fractal dimension. Note that when the mesh size (lattice spacing) goes to zero with the boundaries fixed, the actual density of the clusters, being fractal, goes to zero. The density

we consider is effectively renormalized to remain finite and non-zero in that limit.

For a single anchor placed at x_a on the real axis, the density at a point $z = x + iy$ can be interpreted as the probability that the point z is connected to the point x_a – in other words, it is the two-point correlation function, $\mathcal{P}(z, x_a)$. This quantity is predicted to be given by Kleban et al. (2006)

$$\mathcal{P}(z, x_a) = \frac{c y^{11/48}}{|z - x_a|^{2/3}} \quad (1)$$

where $y = (z - \bar{z})/(2i)$ and c is a non-universal, lattice-dependent constant. It turns out that this density is closely related to that of a dipole in electrostatics – it is $y^{-5/48}$ multiplied by the potential of a dipole, raised to the $1/3$ power.

Figure 1 shows the density contours in a square for single anchors $\mathcal{P}(z, x_a)$ and $\mathcal{P}(z, x_b)$, and for two simultaneous anchors, which corresponds to the three-point correlation function $\mathcal{P}(z, x_a, x_b)$. Now, it was observed that the three-point function is proportional to the square root of the product of the two-point correlation functions and the probability $\mathcal{P}(x_a, x_b)$ that x_a and x_b are connected together (Kleban et al. 2006):

$$\mathcal{P}(z, x_a, x_b) = C \sqrt{\mathcal{P}(x_a, x_b) \mathcal{P}(z, x_a) \mathcal{P}(z, x_b)}, \quad (2)$$

where C is a constant, valid as long as z is at least several lattice spacing from the anchor points x_a and x_b . Near the anchor points for a finite mesh, C is not constant but is a function of x_a, x_b , and z . When z approaches an anchor point, say x_a , it follows (for bond percolation) that $\mathcal{P}(x_a, x_a, x_b) = \mathcal{P}(x_a, x_b)$, and $\mathcal{P}(x_a, x_a) = 1$, so at this point C is identically 1. However, when the mesh goes to zero, C is a constant greater than 1 everywhere else.

Furthermore, rather surprisingly it was found that (away from the anchor points) C was the same for site and bond percolation, with the value $= 1.030 \pm 0.001$, and so appeared to be universal. After these numerical observations were made, it was shown theoretically that (2) indeed follows from conformal field theory

using boundary operators (Kleban et al. 2006), and the constant $C = C_{222}$ is universal and given explicitly by Simmons et al. (2007a)

$$\begin{aligned} C_{222} &= \sqrt{\frac{\Gamma(2/3)^3 \Gamma(5/3)^2}{\Gamma(1/3) \Gamma(4/3)^3}} \\ &= \frac{2^{7/2} \pi^{5/2}}{3^{3/4} \Gamma(1/3)^{3/2}} = 1.02992679 \dots \end{aligned} \quad (3)$$

Excess Number of Clusters

Another example where precise simulations inspired a theoretical result is given by the problems of the *excess* number of clusters (Ziff et al. 1997, 1999). At the critical point, the number of clusters per lattice site n_c is a well-defined, finite, non-universal quantity. This quantity is known exactly for $2 - d$ bond percolation on the triangular and square lattices; for the latter, Temperley and Lieb (1971) found an integral expression for n_c which evaluates simply to $(3\sqrt{3} - 5)/2 = 0.098076211 \dots$ (Ziff et al. 1997). Counting the critical clusters N_c on finite lattices of size $W \times H$ with periodic boundary conditions, it was observed that

$$N_c = n_c HW + b(W/H) + \dots \quad (4)$$

where $b(r)$ is a universal quantity that is a function of the aspect ratio $r = W/H$ but independent of the underlying percolation type (in contrast to n_c , which is not universal and varies from system to system). The universality of $b(r)$ was shown to follow as the singular part of the free energy (Aharony and Stauffer 1997), and $b(r)$ has been calculated exactly for some geometries. For example, in the limit that $r \gg 1$, that is, for a cylinder, $b(r)$ is proportional to r and is given simply by Kleban and Ziff (1998)

$$b(r) \sim \frac{5}{8\sqrt{3}} r. \quad (5)$$

This result valid for all forms of critical $2 - d$ percolation and is reminiscent of (but not identical

to Hu et al. (2000)) the number of wrapping critical clusters in a cylindrical system of length $r \gg 1$:

$$N_{\text{wrap}}(r) \sim \frac{1}{\sqrt{3}} r. \quad (6)$$

The universality of the excess cluster number also applies in higher dimensions, although no theoretical results are known there.

Finding p_c from the Leath Method

The Leath method can be used to generate single clusters in an empty lattice and find an unbiased measure of the size distribution. Say the procedure is started on a single seed. If the cluster grows to a size greater than or equal to some cutoff value s_{max} , it is stopped. The cutoff is chosen sufficiently small so that the growth will always stop before the boundaries of the lattice are reached. In that case, the statistics of the upper cumulative size distribution are unbiased by any boundary effects, and the only finite-size effects are those imposed by the cutoff value.

We define as usual

$$n_s(p) = \text{the number of clusters containing } s \text{ sites, per lattice site} \quad (7)$$

then it follows that

$$P_s(p) = s n_s(p) = \text{the probability that a given site belongs to a cluster containing } s \text{ sites} \quad (8)$$

and

$$P_{\geq s}(p) = \sum_{s' \geq s} s' n_{s'}(p) = \text{the prob. that a given site belongs to a cluster containing } s \text{ or more sites.} \quad (9)$$

Here we are considering bond percolation; if it were site percolation, there would be an extra factor of p in P_s and $P_{\geq s}$ reflecting the probability that the

selected site is an occupied one. The quantity $P_{\geq s}(p)$, unbiased for all $s < s_{\text{max}}$, is determined directly by the growth of single clusters.

According to the usual scaling theory, in the scaling limit where $s \rightarrow \infty$ and $z = (p - p_c)s^\sigma$ is held constant,

$$n_s(p) \sim c_0 s^{-\tau} f(c_1 (p - p_c) s^\sigma) \quad (10)$$

where c_0 and c_1 are the non-universal metric factors, while the exponents τ and σ , and the scaling function $f(z)$, are universal. (This scale variable z should not be confused with the complex coordinate z above.) To define c_0 and c_1 uniquely, one can assume for example $f(0) = 1$ and $\int_{-\infty}^{\infty} f(z) dz = 1$. It follows from (10) that

$$P_{\geq s}(p) \sim \frac{c_0}{\tau - 2} s^{2-\tau} g(c_1 (p - p_c) s^\sigma) \quad (11)$$

where $g(z) = [(\tau - 2)/\sigma] z^{(\tau-2)/\sigma} \int_z^\infty \zeta^{(2-\tau)/\sigma-1} f(\zeta) d\zeta$ for $p > p_c$, and similarly for $p < p_c$. Now it follows that if $f(z)$ is analytic near $z = 0$, then $g(z)$ is also, and we can carry out a Taylor-series expansion, yielding

$$P_{\geq s}(p) \sim s^{2-\tau} (A + B(p - p_c) s^\sigma + \dots) \quad (12)$$

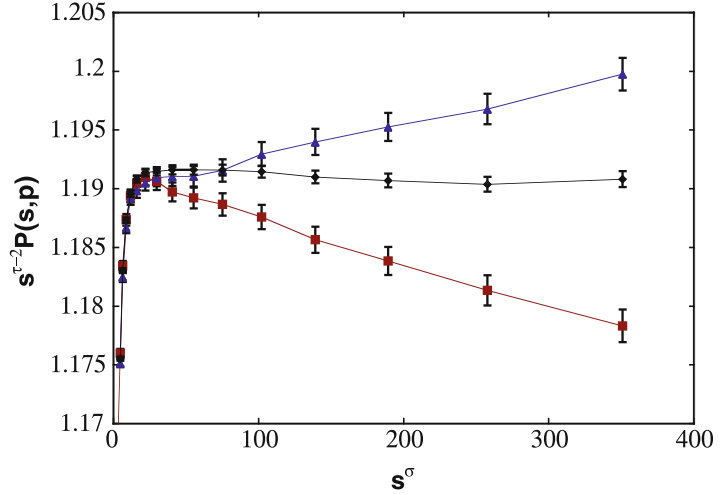
where A and B are constants. Thus, a plot of $s^{\tau-2} P_{\geq s}(p)$ vs. s^σ should give a straight line with a slope proportional to $p - p_c$.

p_c for the hcp and fcc Lattices

We illustrate this method for 3-d site percolation on the hcp and fcc lattices, from Lorenz et al. (2000). The lattice size was 2048^3 , created by using a virtual-memory scheme (Ziff et al. 1984) that only assigns physical memory to cubes of the space as the clusters grow into them, which works well for the growth method because only a small fraction of the lattice is accessed by an individual cluster. The cutoff was $s_{\text{max}} = 2^{21} = 2,048,576$. The exponents τ and σ are

Efficient Simulation of Percolation Lattices,

Fig. 2 Single-cluster growth statistics for site percolation on the hcp lattice, with $p = 0.1992600$, 0.1992555 , and 0.1992500 (top to bottom). Here $P(s, p) \equiv P_{\geq s}(p)$. (From Lorenz et al. (2000))



known exactly in two dimensions but not three, and by fitting the data to (12), those exponents can be found by this method as well. In Fig. 2, we show a plot of $s^{\tau-2} P_{\geq s}(p)$ vs. s^{σ} for three close values of p , using $\tau = 2.189$ and $\sigma = 0.455$. These exponent values were consistent with this data and also that of other 3-d systems, and compare with the values $2.18906(8)$ and $0.4522(9)$ respectively found by Ballesteros et al. (1999), and $2.18958(9)$ and $0.4535(2)$ by Deng and Blöte (2005). The plot shows clearly that for large s , the behavior predicted by (12) is well followed. For s less than about 1000, there are significant deviations due to the finite-size effects of the lattice discreteness. These finite-size effects at p_c can be fit asymptotically by an equation of the form $P_{\geq s}(p_c) \sim s^{\tau-2} (A + Cs^{-\Omega})$ with $\Omega \approx 0.64$ (Lorenz and Ziff 1998).

First the simulations were run at the two outside values of p , and then (12) was used to extrapolate $p_c = 0.1992555$, which was then verified by a third run at this value, which is seen to be horizontal (for large s) in the plot. Analyzing the errors yields $p_c = 0.1992555(10)$. A similar calculation for the closely related fcc lattice yields the slightly but statistically significant lower value $p_c = 0.1992365(10)$. For bond percolation, however, the thresholds for these two lattices at this level of precision are the same $p_c \approx 0.120164$, although they are likely to be different if measured to higher precision. Clearly, a very sensitive

method, like the one presented here, is needed to distinguish such close thresholds.

Another application of single cluster growth has been to find amplitude ratios of the mean cluster size an equal distance below and above p_c , yielding a value $\Gamma^-/\Gamma^+ = 163$ in $2-d$ (Jensen and Ziff 2006), much more precise than earlier determinations, and confirmed by high-order series expansions (Jensen and Ziff 2006). Finally, we note that a similar method of analysis has been applied to directed percolation in 2+1 dimensions (Perlsman and Havlin 2002) leading to the determination of the threshold and critical exponents to higher accuracy than previous works (Grassberger and Zhang 1996; Voigt and Ziff 1997).

Hull Walks and Hull-Generating Walks

The hull in two-dimensional percolation is the boundary between occupied and vacant “perimeter” sites of a percolation cluster. A typical cluster has both external and internal hulls, and an infinite cluster at the critical point has an infinite number of hulls within hulls. The fractal dimension of critical hulls was first conjectured (based upon simulations) to be simply $7/4$ (Sapoval et al. 1985), and then this conjecture was proven theoretically first from field theory (Saleur and Duplantier 1987) and more recently using Stochastic Loewner Evolution (SLE) (Smirnov and Werner 2001).

The “accessible” or Grossman–Aharony hull is the hull (not necessarily external) in which closed-off inlets or “fjords” are bridged and the hull shortened (Grossman and Aharony 1984). It turns out that this hull is also a fundamental measure of percolation clusters and at the critical point has a fractal dimension of $4/3$, identical to self-avoiding walks and the hulls of simple Brownian motion.

Hull-Walk Algorithm

Hulls can be identified on an existing percolation cluster by carrying out a walk that follows the edges of the cluster, as first studied by Voss (1984). On the other hand, just like in the cluster growth algorithm, one can start with an unvisited (undetermined) lattice and decide upon the occupancy of the sites or bonds as they are encountered, and thus generate the hull at the same time as it is being identified. This idea was proposed for site percolation on the square lattice in Ziff et al. (1984), site percolation on the triangular lattice in Weinrib and Trugman (1985), and bond percolation on the square lattice in Grassberger (1986).

For bond percolation, the easiest formulation of the walk is to follow a path that jumps between the centers of the occupied and vacant bonds on the perimeter – or, equivalently, between the bonds on the lattice and the dual lattice. For bond percolation on a square lattice, the paths also follow a square lattice, rotated at 45° from the bond lattice. When an occupied bond is encountered, the walk turns clockwise, while when a vacant bond (or bond on the dual lattice) is encountered, it turns counter-clockwise.

In the hull-generating procedure, when an UNVISITED bond is encountered, that bond is made OCC with probability p and the walk turns clockwise, and made VAC with probability $1 - p$, and the walk turns counter-clockwise. When an already visited site is encountered, the walk turns in such a way that the path always avoids itself. Following is a piece of a program that carries out these steps:

```

dir = 100; x = xo; y = yo;
do
{ x += dx[dir & 3];
  y += dy[dir & 3];
  switch (lat[x][y])
  { case UNVISITED:
    if (random() < probab)
    { lat[x][y] = OCC;
      ++nocc; --dir;
    } else
    { lat[x][y] = VAC;
      ++nvac; ++dir;
    } break;
    case VAC: ++dir; break;
    case OCC: --dir;
  }
} while ((x != xo) && (y != yo)
        && ((dir&3) != 0));

```

(P7)

Here we have rotated the original lattice by 45° so that the walk moves in horizontal and vertical directions and the bonds are effectively on the diagonals. The “& 3” construction is equivalent to “% 4” (modulo 4). The walk ends when it returns to the starting point and it is going the same directions as it started out.

For lattices other than the square one, it is generally convenient to transform the lattice so that it fits on a square one. For example, a triangular lattice can be put on a square lattice with one diagonal bond put in. Then the hull walk has to be constructed between the centers of these bonds, with is rather intricate. An alternative approach is to remain on the simple square lattice with the walk moving in the four diagonal directions, but to make some bonds permanently occupied and/or vacant to simulate the particular lattices. For example, to create a triangular lattice, half of the horizontal bonds, alternating on each row, can be made permanently occupied. Making the same bonds permanently vacant gives the honeycomb lattice, etc.

For site percolation, one can use a variation of the above program in which the walk steps along occupied perimeter sites, always keeping the vacant sites on one side. Details are given in Ziff et al. (1984).

Finding p_c Directly from the Hull-Generating Walk

Starting from an UNVISITED lattice and a single seed, the hull-generating walk above will always

close on itself, forming either external or internal hulls, depending upon the direction of closing. By making a simple hypothesis that at the critical point the internal and external hulls are equally likely (for large hulls), one can deduce an estimate for the critical point. For site percolation on a square lattice this method gave $p_c = 0.59275(3)$ in work from over 30 years ago (Ziff 1986). This approach has not been pursued further, nor have questions of its finite-size effects been explored.

For p away from p_c , the statistics of the internal vs. external hulls will be much different. It was found that the average number of occupied sites in a hull $\langle s_H \rangle$, for site percolation on the square lattice, satisfies (Ziff et al. 1984)

$$\begin{aligned} \langle s_H \rangle_{\text{ext}}^- &\sim \langle s_H \rangle_{\text{int}}^+ \sim A|p - p_c|^{-2} \\ \langle s_H \rangle_{\text{int}}^- &\sim \langle s_H \rangle_{\text{ext}}^+ \sim B|p - p_c|^{-2} \end{aligned} \quad (13)$$

with $A \approx 0.5$ and $B \approx 0.004$, where “int” and “ext” represent internal and external hulls, respectively, and + and – represent above and below p_c , respectively. (The simple exponent -2 above follows from scaling relations of the hull exponents and $D_H = 7/4$ (Weinrib and Trugman 1985; Ziff 1986).) These results imply that the average hull size shows an amplitude ratio of $A/B \approx 125$, reflecting the huge difference between the average size of these two kinds of hulls. While amplitude ratios play an important role in statistical mechanics (Privman et al. 1991), this ratio has not been studied further.

The Enclosed Area Distribution

A more recent application of the hull-generating method has been to find the enclosed area distribution $2 - d$. (Even though both the cluster and the hull are fractal, with dimension $91/48$ and $7/4$, respectively, the area enclosed by a hull is non-fractal and is proportional to the radius squared.) A simple argument from the scaling relation $n_s \sim c_0 s^{-\tau}$, the fractal relation $s \sim A^{D/d}$ and the hyperscaling relation $\tau - 1 = d/D$ implies that, in a critical system of total area A_{tot} , the number of clusters whose enclosed area is greater than A is given by Cardy and Ziff (2003)

$$N_{\geq A} \sim CA_{\text{tot}}/A \quad (14)$$

for A large compared to the mesh area A_0 and small compared to A_{tot} . (For $d > 2$, A represents the volume of an enclosing sphere or rectangular solid, and C is different.) The area distribution can be found from an ensemble of individual closed hulls (loops) generated by the hull-walk algorithm, and it is a simple addition to the program to calculate the enclosed area of the walk on the fly, while the walk is carried out. The coefficient C was found from simulations to be a universal constant $0.022976(5)$, and proven theoretically to be simply (Cardy and Ziff 2003)

$$C = 1/(8\sqrt{3}\pi) = 0.022972037 \dots \quad (15)$$

via a conformal transformation to the problem of the number of clusters wrapping a cylinder given above in (6). Equation (14) represents a completely universal formulation of the size distribution at criticality (in contrast to $n_s \sim c_0 s^{-\tau}$ which involves both the non-universal c_0 , and the non-universal measure of the size, s). Another way to express (14) is in Zipf’s-law form: if you rank-order all the hulls in the system by their enclosed area, then the area of the n th ranked hull is inversely proportional to n and is given by CA_{tot}/n for large A . Other forms of the universal size distribution are given in Ziff et al. (1999).

Applications of the Hull-Generating Walk to Crossing Problems

Hull generating walks can be used to efficiently test for crossing or spanning. For example, consider a rectangular system. A walk is started in the lower left-hand side, and represents the boundary between the occupied bonds above it and the vacant bonds below it. If the walk reaches the right boundary before reaching the top boundary, then there is horizontal crossing, while if it reaches the top before reaching the right-hand side, then there is no horizontal crossing. This process is more efficient than filling the entire lattice with clusters, because only the bonds along the hull are simulated. It allowed a sensitive test (Ziff 1992, 1996) of the finite-size corrections

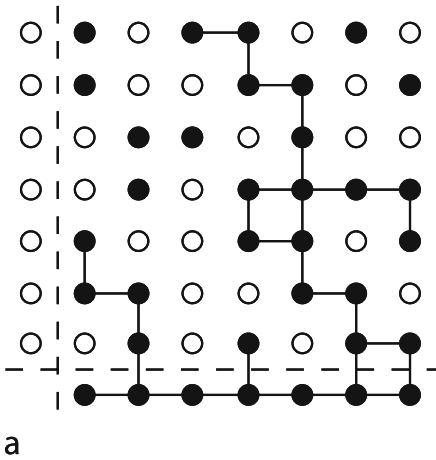
to the crossing probability for a rectangle, which in an important development in percolation theory was found by Cardy to be given by Cardy (1992):

$$\Pi_h(r, p_c) = C_{112}^2 \lambda^{1/3} {}_2F_1(1/3, 2/3; 4/3; \lambda), \quad (16)$$

with $C_{112}^2 = 2\pi\sqrt{3}/\Gamma(\frac{1}{3})^3 = 0.56604668 \dots$, where ${}_2F_1$ is the hypergeometric function and the subscript h signifies the horizontal crossing probability. Here r is the aspect ratio of the rectangle, and is related to λ by $\lambda = ((1 - k)/(1 + k))^2$ and $r = 2K(k^2)/K(1 - k^2)$, where $K(m)$ is the elliptic integral. This parametrization can be simplified to $r = K(1 - \lambda)/K(\lambda)$ and inverted explicitly as Ziff (1995) $\lambda = \vartheta_2^4(\exp(-\pi r))/\vartheta_3^4(\exp(-\pi r))$ where $\vartheta_n(q)$ are elliptic theta functions. Finally, the parameter λ , which represents the cross-ratio of the coordinates of the corners of the rectangle when mapped to the half plane, can be eliminated to yield a closed-form explicit expression for $\Pi_h(r, p_c)$, differentiated with respect to r (Ziff 1995):

$$\begin{aligned} \frac{\partial \Pi_h(r, p_c)}{\partial r} &= -\frac{1}{3} \pi C_{112}^2 \vartheta_1'(e^{-\pi r})^{4/3} \\ &= -\frac{2^{4/3}}{3} \pi C_{112}^2 \eta(ir)^4 \end{aligned} \quad (17)$$

where $\eta(\tau)$ is the Dedekind eta function. Equation (17) implies the series



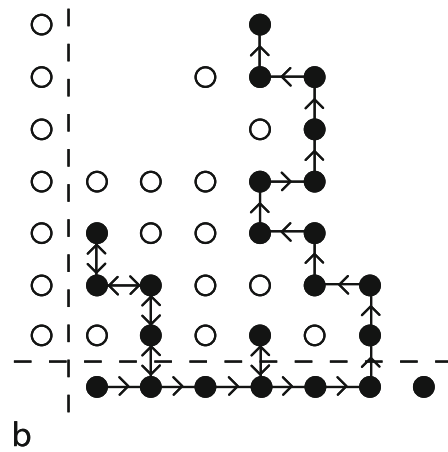
$$\begin{aligned} \Pi_h(r, p_c) &= \frac{2^{4/3} \pi C_{112}^2}{3} \\ &\times \left(e^{-\pi r/3} - \frac{4}{7} e^{-7\pi r/3} \dots \right). \end{aligned} \quad (18)$$

The prediction for $\Pi_h(1, p_c) = 1/2$ for a system with a square boundary for site percolation on a square lattice of size $L \times L$ was verified in Ziff (1992). The hull-walk used in that work is illustrated in Fig. 3, here rotated so that crossing is considered in the vertical rather than horizontal direction. The behavior that crossing translates into the walk hitting one boundary before the other is exactly analogous to problems solved in SLE.

This work showed that the finite-size corrections to $\Pi_h(1, p_c) = 1/2$ are for large systems described by

$$\Pi_h(1, p_c) = 1/2 + 0.319/L + \dots \quad (19)$$

The numerical results were not consistent with a significant contribution from the “irrelevant” scaling variable $L^{-0.85}$ (Ziff 1994) and later it was shown that indeed because of the symmetry of the square system, the irrelevant term does not contribute here (Hovi and Aharony 1996). A consequence of (19) is that several estimates



Efficient Simulation of Percolation Lattices, Fig. 3 Hullwalk for a test for vertical crossing for site percolation on the square lattice. (a) all clusters connecting the bottom to the top. (b) the equivalent hull that would be

generated from the site-percolation hull-generating walk with the same probability. *Solid circles*: occupied sites. *Open circles*: vacant sites. (From Ziff (1992))

of p_c based upon measurements of $\Pi_h(1, p_c)$ do not converge with the usual scaling $\sim L^{-1/\nu}$ but instead with the scaling $L^{-1-1/\nu}$ (Ziff 1992).

The hull method also is very efficient for exact enumeration. Basically, by stepping through every possible hull, one can determine the polynomials for $\Pi_h(r, p)$ as a function of p , for a fixed r and system size. This way $\Pi_h(1, p)$ could be found for square system size $L \times L$ for L up to 7, (Ziff 1992; Ziff and Newman 2002) which would be very difficult to do with a complete exact enumeration, as this would require 2^{49} realizations of the lattice. For the first few values of L , $\Pi_h^{(L)}(1, p)$, written as a series in $p^i q^{L^2-i}$ where $q = 1 - p$, is given by

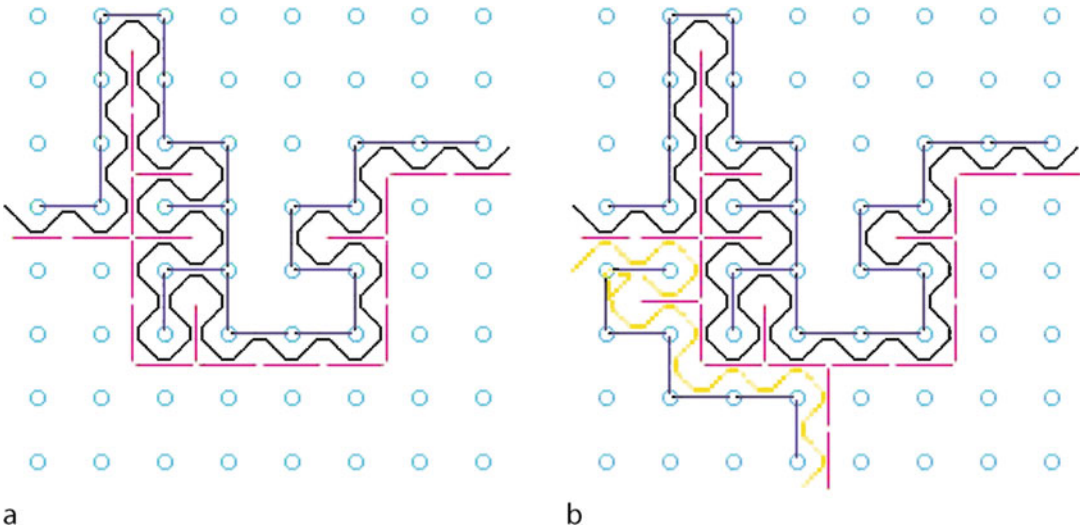
$$\Pi_h^{(2)}(1, p) = 2p^2 q^2 + 4p^3 q + p^4 \quad (20)$$

$$\begin{aligned} \Pi_h^{(3)}(1, p) = & 3p^3 q^6 + 22p^4 q^5 + 59p^5 p^4 \\ & + 67p^6 q^3 + 36p^7 q^2 + 9p^8 q + p^9. \end{aligned} \quad (21)$$

Polynomials for L up to 4 are given in Reynolds et al. (1980) and those for L up to 7 can be found in Ziff and Newman (2002). These results can be used

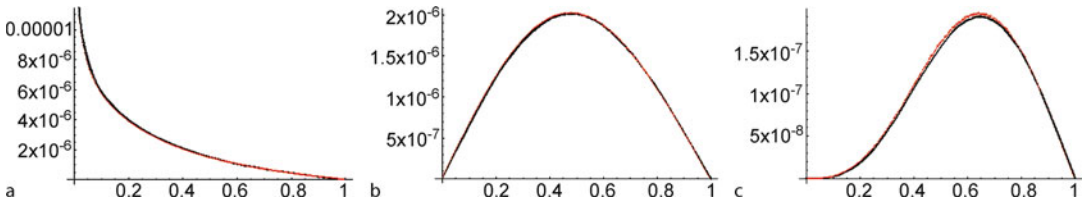
for a variety of studies; for example, looking at the kurtosis of the distribution, it was shown (Ziff 1994) that the distribution of first crossings $(\partial/\partial p) \Pi_h(r, p)$ is not a gaussian curve as had been previously thought. This work was followed by a more general mathematical proof (Berlyand and Wehr 1995) that the tails behave like $\ln[(\partial/\partial p) \Pi_h(r, p)] \sim -L/\xi \sim -L|p - p_c|^{4/3}$ where $\xi \sim |p - p_c|^{-\nu}$ with $\nu = 4/3$ in 2d is the correlation length.

In more recent work (Simmons et al. 2007b), the hull-generating method was used to test a generalization of Cardy's formula that describes the probability density that crossing clusters have lower edges at $y = a$ and $y = b$ on the left and right-hand boundaries, respectively, with various conditions on whether the cluster touches the bottom. Figure 4 shows how this problem is simulated by a hull walk, here for bond percolation with the bonds themselves horizontal and vertical, and the steps along the diagonals. Figure 5 shows excellent agreement between the simulations and the theory. The hull-generating walk proved very efficient for this problem, since walks that hit one of the forbidden boundaries (used to enforce the crossing criteria) were stopped without generating the rest of the hull.



Efficient Simulation of Percolation Lattices, Fig. 4 (a) The hull-generating walk (in black) used to test for a cluster, whose lower edge is half-way up the left-hand side, crossing to the right-hand side, and to find

the distribution of values y for where it hits on the right-hand side. (b) an additional walk (in yellow) to check that there are no other clusters crossing below the given walk. (From Simmons et al. (2007b))



Efficient Simulation of Percolation Lattices, Fig. 5 Measurements (*points*) and theory (*lines*) for the distribution of the lower boundary on the right-hand side, of clusters whose lower boundary on the left-hand side is at $y = 1/2$. (a) Clusters that touch the bottom, (b) no

restriction on the crossing of the clusters, and (c) clusters that cross from left to right but do not touch the bottom, and have no crossing clusters below them. (From Simmons et al. (2007b))

Thus, in a few day's of computer work, it was possible to simulate $3.3 \cdot 10^{11}$ hulls on a lattice of 512×512 bonds, something that would be nearly impossible to carry out if all lattice bonds were considered in the simulation.

Gradient Percolation

Sapoval et al. (1985) first considered percolation in a gradient, and showed that in 2d it is an efficient way to find that percolation threshold (Rosso et al. 1985). In this approach, a rectangular system is set up with a linear gradient in p , going from 0 to 1 as y goes from 0 to 1. There will be a percolating cluster connected to the upper boundary, and the hull of that cluster will sample values of p that are close to p_c . Sapoval et al. (1985) showed that the hull will stay within a relatively small region $L^{4/7}$ of the lattice of inverse gradient $|\nabla p|^{-1} = L$. Therefore, as $L \rightarrow \infty$, the “frontier” will be localized about p_c .

For a finite L , two measures of $p_c(L)$ are (i), the average value of p of all the occupied+vacant sites (or bonds) of the hull, or, (ii) just the fraction of occupied to total bonds along the hull:

$$p_c^{\text{est}}(L) = \frac{n_{\text{occ}}}{n_{\text{occ}} + n_{\text{vac}}}. \quad (22)$$

For large systems (small gradients), these measures should be asymptotically equivalent. Simulating system of size up 1000×1000 for site percolation on the square lattice, Rosso et al. found that the estimates fell on a straight line when plotted as a function of the gradient $1/L$,

with as extrapolated value of $0.592805(10)$, slightly higher than the values we have seen above.

By combining gradient percolation with the hull-generating walk, one can create a very efficient and simple method to determine percolation thresholds in two dimensions (Ziff and Sapoval 1986). Basically, the program (P7) is used, with prob now a function of y , and periodic boundary conditions in the horizontal direction. The “front” (x coordinate) of the walk is kept track of, and when it reaches a new value, the column (all values of y) with the value of x mapped on to the periodic lattice is cleared out and returned to the UNVISITED state. This is allowed because the walk snakes back a maximum distance of the order of its width in the y direction, so that sites or bonds behind that can be forgotten. Thus the simulation runs continuously, effectively simulating an infinitely wide system.

To start the walk, one has to make a vertical column on the left of all occupied sites or bonds above the starting point, and vacant ones below it. This will keep the walk from closing on itself at the beginning. Data from the early part of the simulation can be thrown away to eliminate any bias that it causes.

This method was used to find precise thresholds, some up to seven significant figures, for a variety of two-dimensional lattices, including the Archimedean lattices for site percolation (Suding and Ziff 1999), and the kagomé lattice for bond percolation (Ziff and Suding 1997). These results are useful for understanding how thresholds depend upon the lattice structure, and to test conjectures for the values of the thresholds (see Scullard and Ziff 2006).

The question of the convergence of the estimates is open: for many systems, the convergence behavior seems to change from $1/L$ for smaller L to a different behavior (or perhaps the same $1/L$ behavior but with a different coefficient) for larger L . In fact, for site percolation on the square lattice, it turns out that the linear behavior seen by Rosso et al. breaks down for L larger than about 1000, and the curve levels off, extrapolating to a value ≈ 0.5927465 , close [to that] found by other methods. The understanding of the convergence of this method remains an open problem.

The errors can be determined easily by looking at batches of results, and are proportional to $(n_{\text{occ}} + n_{\text{vac}})^{-1/2}$. The proportionality constant is of order 1, indicating a very efficient method, and grows slowly with increasing L , implying that with increasing L , somewhat more work is needed to achieve the same level of precision.

Example: The Critical Surface for the Checkerboard Lattice

As an example of this method, we consider the checkerboard lattice, that is a square lattice with four different probabilities p_1 , p_2 , p_3 , and p_4 around each colored square. According to a conjecture by Wu concerning the more general q -state Potts model, here specialized for $q = 1$, the critical surface satisfies the formula (Wu 1979)

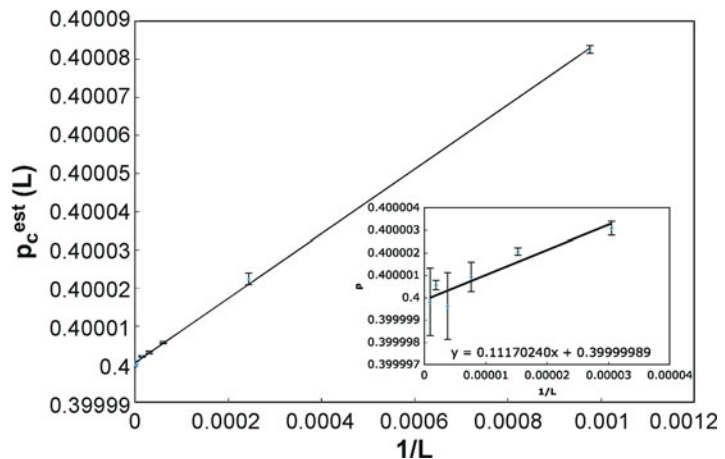
$$1 - (p_1 p_2 + p_1 p_3 + p_1 p_4 + p_2 p_3 + p_2 p_4 + p_3 p_4) + p_1 p_2 p_3 + p_1 p_2 p_4 + p_1 p_3 p_4 + p_2 p_3 p_4 = 0. \quad (23)$$

This result does not appear to follow directly from duality, in contrast to all other exact results known in percolation (Sykes and Essam 1964; Wierman 1984; Ziff and Scullard 2006). However, it reduces to the known exact results for the inhomogeneous honeycomb lattice (letting $p_4 = 0$), the inhomogeneous triangular lattice (letting $p_4 = 1$), and the dual checkerboard lattice ($p_2 = 1 - p_1$), and duality in the sense that $p_i \rightarrow 1 - p_i$ also satisfies this formula. It is the most general relation of this form, linear in all of the individual probabilities, that satisfies these requirements, but there is no obvious reason why it has to be linear in this way.

It seems that this result has not been tested numerically in the past. Here we investigate one case $p_1 = 73/90 = 0.811111\dots$, and $p_2 = p_3 = p_4 = p$ using the hull-gradient method. According to the conjecture (23), p should equal 0.4 exactly.

In order to test this prediction, we fix the value of p_1 on every fourth bond, while for the rest of the bonds we allow p to follow the gradient, and use the n_{occ} and n_{vac} for these bonds to estimate the critical value of p by (22). Figure 6 shows the plot of $p_c^{\text{est}}(L)$ that follows for different values of the inverse gradient $1/L$. The lattice was $16,384 \times 16,384$, but we were able to go to inverse

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Fig. 6 Results of gradient percolation study for the checkerboard lattice with $p_1 = 73/90$, and $p_2 = p_3 = p_4$ predicted to be 0.4 by (23). (From Scullard and Ziff (2008))



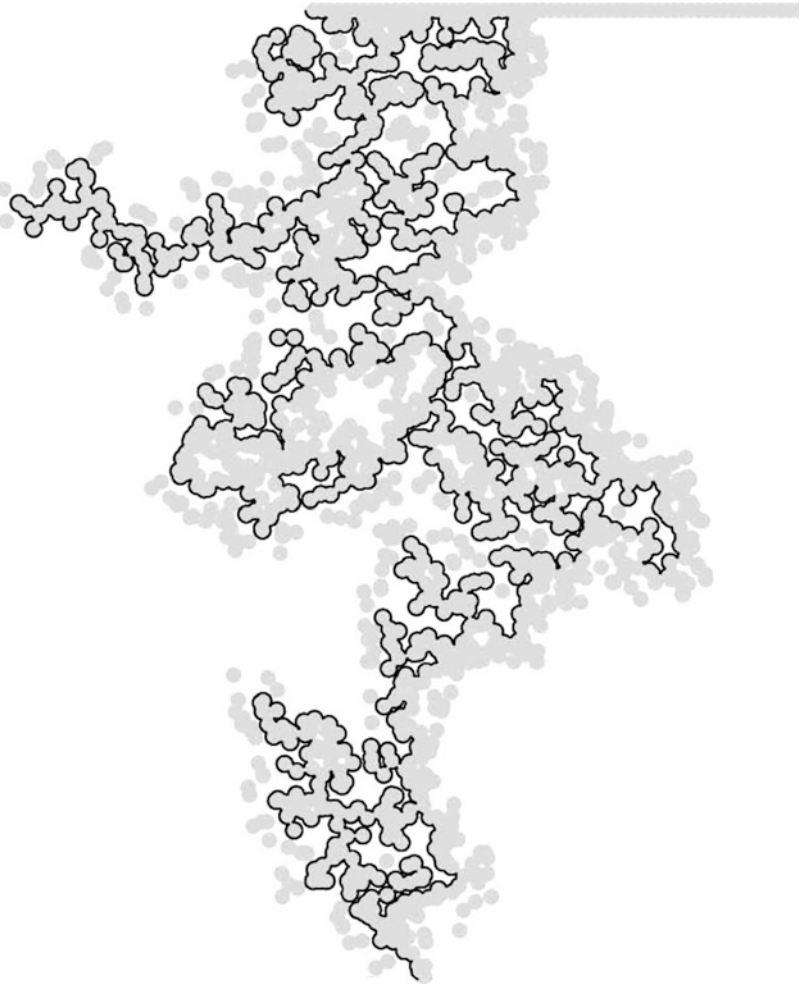
gradients as large as $L = 524,288$ without having $y_{\max} - y_{\min}$ or $x_{\text{front}} - x$ exceed 16,384. We also used a periodic scheme in the vertical direction in order to have the walk automatically adjust to its own position. In this particular case, the linear dependence of p_c^{est} upon the gradient $1/L$ seems to hold, with an extrapolated value of 0.39999989(20). To achieve these very small error bars, a total of $n_{\text{occ}} + n_{\text{vac}} = 10^{14}$ random numbers were generated, one for each time the walk encountered an unvisited bond whose state was not previously determined. Thus, Wu's conjecture is numerically confirmed to high accuracy for this point. Additional points are tested in Scullard and Ziff (2008).

The hull-gradient method has been generalized to continuum percolation, illustrated in Fig. 7, yielding the most precise known value for the fractional critical coverage $\phi_c = 0.6763475(6)$ (Quintanilla et al. 2000; Quintanilla and Ziff 2007).

Note, when doing work like this, it is imperative to use a high-quality random number generator, and not ones typically incorporated in computer languages or compilers. For much of our own work reviewed here, we used a four-tap shift-register sequence random number generator based upon the exclusive-or operation, with maximum lag of 9689 and cycle $2^{9689} - 1$ (Ziff 1998).

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Fig. 7 Frontier (hull) of the percolating region for the continuum percolation of overlapping disks in a gradient in the horizontal direction. (From Quintanilla et al. (2000))



Simulating the Grossman–Aharony Accessible Hull

It does not seem possible to make a random walk process that generates the accessible hull of a percolation cluster (the hull in which all “fjords” are closed off) directly, because of the long range correlations. However, it is possible to generate this hull by carrying out two walks: the first to generate say the outside hull of a cluster, and then a second walk that encircles the first, and can jump across the fjords. In this way, samples of a walk that are equivalent to the two-dimensional self-avoiding walk can be generated easily.

In the same way, a second walk can be added to gradient percolation (delayed behind the first walk by the correlation length), and the second walk will trace out the accessible hull of the frontier in the gradient. In this, way, an infinitely long accessible hull can be made (essentially one dimensional, however, because of the effect of the gradient).

The Microcanonical-Canonical Method

Here we discuss the method of Newman and Ziff (2000) to simulate percolation that, unlike other methods considered so far, allows one to simulate problems for all values of p through one simulation.

The idea is to start with an empty lattice, and add one site or bond at a time, and update the cluster connectivity on the fly, somewhat like the Hoshen–Kopelman method, but applied to clusters rather than rows. The quantity of interest is stored as a function of n , the number of added sites or bonds. Call this quantity Q_n , which represents the fixed- n , or “microcanonical” value of Q . Then, for a given probability, the “canonical” $Q(p)$ follows from convolving with the binomial distribution

$$Q(p) = \sum_{n=0}^N \binom{N}{n} p^n (1-p)^{N-n} Q_n, \quad (24)$$

where N is the total possible number of sites or bonds in the system. Note that these approaches

have also been described as “canonical” and “grand-canonical”, by considering s as representing the number of particles in the system (Shchur 2000). Here, we are thinking in energetic terms, along the lines of the Potts model representation of percolation.

An example of this has already effectively been given above in the $p^n q^{N-n}$ series of $\Pi_h^{(L)}(1, p)$ (20) and (21), with $N = L^2$. Consider the case $L = 2$, and let $Q(p) = \Pi_h^{(2)}(1, p)$. The coefficients in (20) are precisely the number of ways of having horizontal crossing with n occupied sites and $N - n$ vacant sites. Because there are $\binom{N}{n}$ possibilities of having n sites in the system, it follows that the Q_n are just these coefficients divided by $\binom{N}{n}$. Therefore, for this system $Q_0 = Q_1 = 0$, $Q_2 = 1/3$, and $Q_3 = Q_4 = 1$ (the latter reflecting the fact that with three or four occupied sites, there will always be crossing). Then, the convolution in (24) is formally identical to $\Pi_h^{(2)}(1, p)$ given in (20).

The antecedents of this method in the literature are many. The idea of extrapolating results of simulations to different values of p is reminiscent of the histogram method (Hu 1992). The representation of clusters as a tree structure and some of the update bookkeeping steps are reminiscent of the Hoshen–Kopelman method (Hoshen and Kopelman 1976). Similar tree structure representations of clusters have been used in kinetic gelation models (de Freitas and Lucena 2000). Finally, the idea of adding one occupied site or bond at a time was suggested in a problem in Gould and Tobochnik (1996). But (Newman and Ziff 2000) seems to be the first place that all these ideas were put together along with the convolution (24) and used to find results for some quantity for all values of p . These ideas have been incorporated in an extensive discussion of this method in Gould et al. (2006).

For definiteness we consider bond percolation. Initially, no bonds exist, and all sites are clusters of size one and each has a different label. (Again, the size is the number of sites the cluster contains). When a new bond is added, it can either connect sites belonging to the same cluster, in which case

nothing needs to be done, or it can connect sites from two different clusters. In the latter case, these two clusters are combined into one by a union operation. For efficiency, the smaller cluster is incorporated into the larger one.

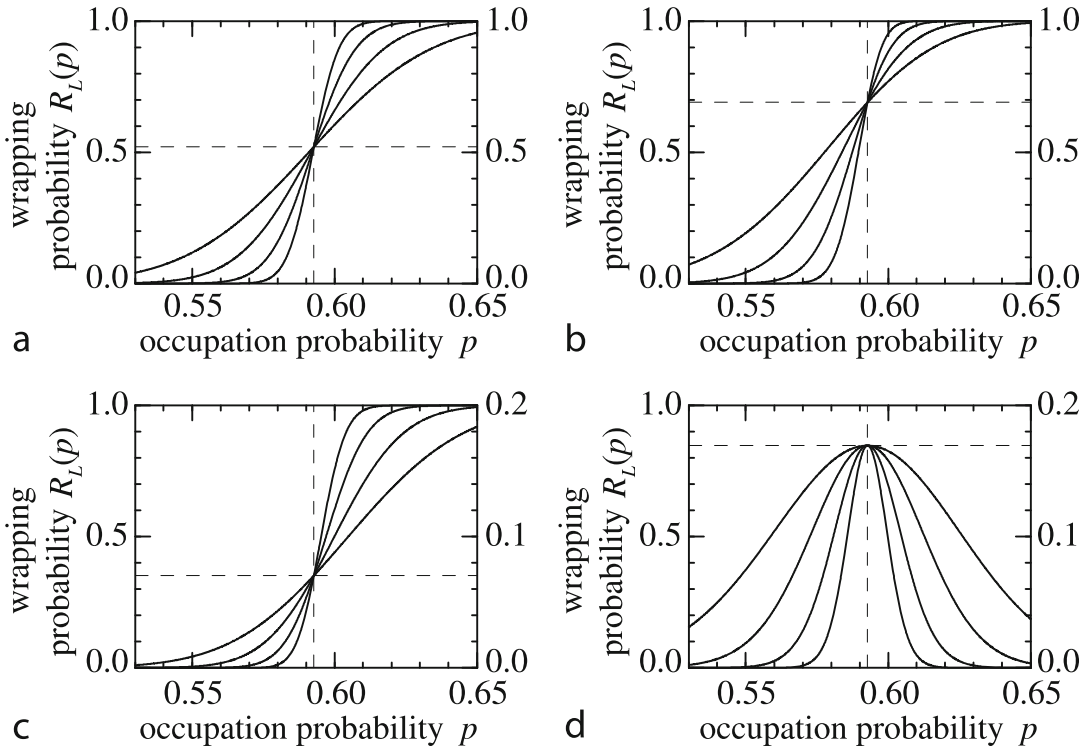
A simple approach to carry out this operation is to label each site of the lattice by an index representing the cluster it belongs to, and having a look-up table that registers the number of sites in each cluster. When a new bond connects sites of two different indices, the look-up table tells which of the two is smaller, and then a neighbor search like (P2) or (P3) can be used to relabel all sites of the small cluster to the index of the larger cluster. The appropriate updates to the look-up table are then made.

However, this method is somewhat slow because a given site is relabeled several times, and it can be improved by having a cluster remembered as a tree structure and linking the root of the smaller cluster to that of the larger one, as shown in Fig. 8.

Here we describe a recursive program to carry out the “union-find” operation for bond percolation. More details are given in Newman and Ziff (2001), which discusses the algorithm for site percolation.

First of all, in contrast to the programs given above, here we use a one-dimensional array `ptr[r]` to represent a system of any dimensions. An array `nn[i][dir]` is constructed ahead of time that tells the nearest-neighbors of every point `i` in the system, and thus can be set up for any boundary condition. This array is only used to decide which pair of sites a given bond connects. Sites are indexed with a single signed integer label for speed, taking values from 0 to $N - 1$.

The array `ptr[]` serves triple duty: for non-root occupied sites it contains the label for the site’s parent in the tree (the “pointer”); root sites are recognized by a negative value of `ptr[]`, and that value is equal to minus the size of the cluster;



Efficient Simulation of Percolation Lattices, Fig. 8 Wrapping probabilities $R_L(p) \equiv \Pi_{\text{wrap}}(p_c)$ calculated using the Newman–Ziff algorithm, for $L \times L$ tori with $L = 32; 64; 128$, and 256 , for wrapping (a) along a

specified axis, (b) along either axis, (c) along both axes, and (d) along one axis but not the other. The dotted lines denote the expected values of p_c and $\Pi_{\text{wrap}}(p_c)$. The curves are sharper as L increases. (From Newman and Ziff (2000))

for unoccupied sites `ptr[]` takes the value `EMPTY`, which is defined as some value such as $-N - 1$ that is never reached by any of the roots.

We define a function which performs the “find” operation, returning the label of the root site of a cluster, as well as accomplish path compression. The version we use is recursive:

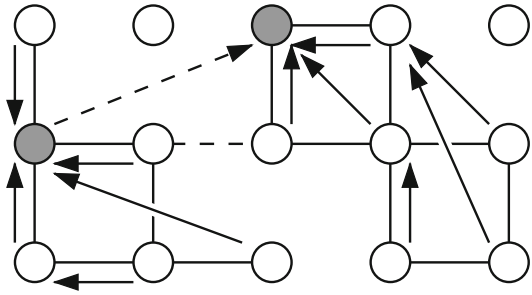
```
int findroot (int i)
{
  if (ptr[i] < 0) return i;
  return ptr[i] = findroot (ptr[i]);
}
```

When the recursion is “unwound”, all the sites of the links are relabeled to point to the new root. This seems to result in an optimal amount of relabeling to make this process run quickly.

The code to perform the actual algorithm is quite brief. Ahead of time, an ordered list of all the bonds is made. A given new bond connects the two neighboring sites `s1` and `s2`. The function `findroot()` is called to find the roots of each of the two sites. If amalgamation is needed, it is performed in a weighted fashion, smaller clusters being added to larger (bearing in mind that the value of `ptr[]` for the root nodes is *minus* the size of the corresponding cluster). Following is the main code to accomplish that:

```
r1 = findroot (s1);
r2 = findroot (s2);
if (r2 != r1)
  if (ptr[r1] > ptr[r2]) {
    ptr[r2] += ptr[r1];
    ptr[r1] = r2;
  } else {
    ptr[r1] += ptr[r2];
    ptr[r2] = r1;
  }
```

There are also easy techniques to check for crossing or wrapping during this process. One stores the number of such events as a function of n , the number of bonds put down, and then uses the convolution (24) to find the desired quantity as a function of p . Of course, the procedure must be repeated many times to get good statistics for all n . The result of a test of wrapping around a torus is given in Fig. 9.



Efficient Simulation of Percolation Lattices, Fig. 9 Tree data structure, shown the merging off the cluster of six sites on the left with the cluster of seven sites on the right, due to the addition of the new bond (dashed bond). Arrows show the directions of the links. (From Newman and Ziff (2000))

The main point of this algorithm is that it can find the Q_n in a time that is very nearly linear in the number of lattice sites. Once the Q_n are found and stored in an appropriate array, they can be used to find various properties of the system for any p .

Other Numerical Techniques

In this section we briefly mention some other numerical techniques that have been applied to percolation.

The Binary Search Method

In this method, a random number p_i uniform in $(0, 1)$ is assigned to each site (say) of the lattice. One chooses a value of p such that sites with $p_i < p$ are assumed to be occupied, and checks for percolation. By making a binary search up and down in p (with the same p_i assigned to each site), in about 20 steps the probability where that particular sample first percolates can be found to six significant digits. Repeating this for many samples and averaging the results yields the *average* estimate for p_c .

If horizontal crossing is used for the criterion for percolation, then this average corresponds to $\int_0^\infty p(\partial/\partial p) \Pi_h(p, r) dp$. When systems of different sizes are simulated,

finite-size scaling of this quantity can be used to extrapolate the estimate to $L \rightarrow \infty$. In general, finite-size scaling implies that estimates converge to p_c as $L^{-1/\nu}$ (Stauffer and Aharony 1994), but for certain symmetric systems, such as a square boundary for site percolation on a square lattice, the convergence goes as $L^{-1/\nu-1}$ (Ziff and Newman 2002) and even faster for wrapping around a periodic system (Newman and Ziff 2001).

This method is quite efficient in finding p_c since for a lattice of $N = L^2$ sites, the total amount of time to measure one sample grows only as $N \ln N$. It has been used in numerous studies of percolation in various dimensions (Stauffer and Aharony 1994).

Lattice-Less Methods

Vollmayr (1993) introduced the idea that by using a kind of random number generator (effectively a very non-linear function) that takes as an input the coordinates of a site, and outputs a uniform random number that has no correlations with the random numbers that results from one of the neighbors, one does not have to remember the occupancy state of a given site. However, for most problems, one does have to remember whether that site has been visited (or checked as in the cluster algorithms), so techniques to remember the latter have to be used, some of which are discussed in Paul et al. (2001). There are several problems where one does not need to remember which sites have been visited, so for these problems this technique is particularly memory efficient. One example is the problem of finding the enclosed area of a hull-generating walk: here it is not necessary to remember if a site have been visited or not, and the method can be used to simulate any size system. Another example is just finding the end-to-end length of a very long walk, for a fractal measurement. One is only limited by the computational time available.

A drawback of this method is that it requires this special type of random number generator. Vollmayr uses a generator related to data encryption, which evidently has the necessary

properties and is sufficiently uncorrelated and fast (though not as fast as typical random number generators used for Monte Carlo simulations). However, more work needs to be done to study this generator's quality for these types of problems.

Osterkamp et al. (2003) introduced a related idea, using the feature of congruential random number generators that one can jump ahead or behind any number of steps in the random number sequence by making an appropriate modification to the multiplier. Using this they were able to simulate diffusion on percolation clusters on high-dimensional (virtual) lattices as large as $420^7 \approx 2.3 \cdot 10^{18}$ sites. This is another problem for which there is no need to remember which site has been visited before, so no list is needed, and the program required very little memory.

Conductivity and Backbones

An important application of percolation is to flow and resistance problems. The conductivity of a percolating network (say with occupied bonds replace by identical resistors) goes to zero as the percolation threshold is approached from above, and much work has been done in studying that process. The simulations are based upon solving Kirchhoff's equations around each vertex of the lattice.

When considering conductivity of a percolation cluster, the role of different bonds becomes evident. One can define conductivity between two points far apart in a cluster, or alternatively between two opposite edges of a bounded system (the "bus-bar" problem). In either case there will be a backbone that carries the current, and dangling ends that are only singly connected to the backbone, which can be removed. Within the backbone, bonds can be classified into different categories, with the "red" bonds being ones the "hottest" in that cutting any one of them will break the flow of current (Pike and Stanley 1981).

To find the backbone, several methods have been used, including Tarjan's method (Tarjan

1972), burning algorithms (Herrmann et al. 1984b), and matching algorithms (Moukarzel 1998). Grassberger has introduced an efficient hull-walk based algorithm which however works only in two dimensions (Grassberger 1992). Once the backbone is found, the conductivity can be estimated efficiently in 2d by the algorithm of Lobb and Frank (1984), which reduces the lattice by successive use of a star-triangle transformation, or in general by finite-element methods to solve the Kirchhoff equations. Conductivity can also be studied by considering the properties of random walks on the percolation cluster (Hong et al. 1984).

In 2d at the critical point, the backbone has a fractal dimension $D_b = 1.6432(8)$ (Grassberger 1999) or $1.6434(2)$ (Deng et al. 2004) such that in a system of length scale L , the number of backbone bonds grows as L^{D_b} . The red sites scale simply as the inverse of the correlation-length exponent, $D_{\text{red}} = 1/\nu$ (Coniglio 1982), which equals $3/4$ in 2d. The conductivity at the critical point scales with the system size as L^t with $t/\nu = 0.9826(8)$ (Grassberger 1999). At one time there was a great deal of interest in studying this exponent because of the Alexander–Orbach conjecture (Alexander and Orbach 1982) that t/ν was equal to 1, which however was proven (numerically) to be incorrect in five back-to-back papers in Physical Review B in 1984 (Herrmann et al. 1984a; Hong et al. 1984; Lobb and Frank 1984; Rammal et al. 1984; Zabolitzky 1984).

Conclusions

This article describes a number of algorithms and programming techniques to study cluster statistics, crossing problems, area distributions, etc. of percolation. By no means did it cover all of them; having been a very active field of research for 50 years, there are many other methods and techniques that have been proposed and studied. Some applications of numerical techniques are also presented.

An example of the development of the substantial numerical work done in this field is provided by the determination of the threshold for site percolation on the square lattice, whose value has not been derived theoretically and must be found by simulation. After starting out

at 0.581(15) in 1961 in the first Monte-Carlo determination (Frisch et al. 1961), and after dozens of advances in the following three decades, by the early 1990s the six-digit value 0.592746 was achieved (Ziff 1992). Yet, in the 16 years since then, while that value has been confirmed, the seventh digit still has not been agreed upon – the various determinations, many quoted above, fall in the range 0.5927460–0.5927466. Although one might think that with all the advances in computer power and algorithms that have occurred over these years, it would have been fairly easy to extend this result further, it turns out to be harder than might have been anticipated, because of uncertainties in the finite-size corrections and in the quality of random-number generators, which seem to be significant at this level of precision. Such high precision values are in fact necessary for precise studies of critical behavior, where simulations involving 10^{13} – 10^{14} sites are not uncommon, and in 2d, site percolation on the simple square lattice remains one of the most popular models for various reasons, despite of the fact that exact thresholds are known for other $2 - d$ system.

Future Directions

Work in this field remains quite active and there are many interesting questions that are still unanswered. Convergence of many of the estimates, precise values of sub-leading (including irrelevant) exponents, more accurate calculation of the scaling functions and amplitude ratios are some such questions. For percolation thresholds, continued study of thresholds can perhaps lead to new exact results and in any case can help advance the understanding of why particular lattices have the thresholds that they do. The combination of the efficient techniques that have been developed and improved upon over the years and the availability of powerful computers should allow many of these questions to be investigated fairly easily today. Here is a sampling of some specific questions for future study based upon the work discussed above:

- In the Newman–Ziff study of percolation around tori, it was found that the wrapping probabilities (for various situations, such as “either” or “one-way”) approach their theoretical values (Pinson 1994) as L^{-2} , implying that the estimates for p_c converge to the actual value as $L^{-11/4}$. However, no theoretical justification was found for this result. Note that additional numerical work showing fair agreement with this scaling for a variety of lattices was done by Parviainen (2007).
- As mentioned above, the estimate of p_c for the hull-gradient method seems to converge as the reciprocal of the gradient for many systems (as in Fig. 6), while in others it changes its behavior and even is non-monotonic. Additional precise measurements, including tests with different random number generators, on a variety of systems can help elucidate this question. Another interesting question is the effect of the angle of the gradient with respect to the axis for various lattices. Some work along these lines for the kagomé lattice was done in Suding and Ziff (1999).
- When written in terms of the enclosed area distribution, the size distribution follows the Zipf’s-law form (15) above which is an entirely universal form with no metric factors. Only preliminary studies have been made on this quantity away from p_c , and a simple exponential scaling curve is possibly seen (Ziff 2004). Clarification of this behavior (and in relation to the Kunz–Souillard (1978) form of the percolation scaling function which predicts exponential behavior in the size, not the area) is needed. Note there are other measures of the area that can be used, such as that of the enclosing Grossman–Aharony hull, that would also be interesting to study.

Further interest in percolation by mathematicians, following the developments in Stochastic Loewner Evolution, will undoubtedly lead to many more simulation studies and new algorithms in percolation, such as Gamsa and Cardy (2007) which concerns geometry of clusters on the closely related Potts model. It is interesting to note that in the percolation case, SLE develops a

theory for the continuum limit of precisely the hull walks which were first introduced as a computational technique in this field more than three decades ago (Grassberger 1986; Weinrib and Trugman 1985; Ziff et al. 1984).

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Scaling Theory of Percolation Clusters

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Article Outline

Introduction
Theoretical Methods and Computer Simulation
Mean-Field Approximation
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The Hoshen-Kopelman Algorithm
Relation to Ising and Potts Models
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Introduction

In 1941 Paul Flory, who later received the Chemistry Nobel prize in 1974, published (Stauffer 1979) the first paper on percolation theory

(Essam 1980; Stauffer and Aharony 1994; Sahimi 1994; Grimmett 1999; Flory 1941) (although he did not use the standard terminology of percolation) to describe the vulcanization of rubbers. Later on, others applied and generalized the theory, in particular by developing percolation theory on lattices and studying it by computer simulations. Most of the theory presented in this chapter was known around 1980, though in the case of the results obtained by computer simulations they were less accurate than today. But on the questions of the universality, of critical spanning probability, and of the uniqueness of infinite (sample-spanning) clusters, papers published in the 1990s showed that some of the earlier results were wrong. Even today it is questioned by some whether the critical exponents of percolation theory can be applied to real polymer gelation, the application that Flory had in mind 78 years ago.

To describe percolation and its relation to vulcanization, consider a large lattice in which we assume that each site is independently and randomly occupied with probability p and empty with probability $(1 - p)$. Depending on the applications, other words or terminology may be used, instead of occupied and empty, e.g., Republican and Democrat for the majority party in an electoral districts of the United States. A cluster is then defined as a set of occupied neighboring sites. Percolation theory deals with the number and structure of such clusters as a function of their size s , i.e., of the number s of the occupied sites in the cluster. In particular, it asks whether an infinite cluster spans from one side of the lattice to the opposite side. Alternatively, and more naturally, if one wants to describe chemical reactions for rubber vulcanization, site percolation problem can be replaced by bond percolation in which all the sites are occupied, but the links or bonds between neighboring sites are either present (or occupied) with probability p or absent (or unoccupied) with probability $(1 - p)$, independently and randomly. A cluster is then a set of neighboring sites connected by occupied links or bonds, and the size s of the cluster is counted as the number of links or the number of

Professor Dietrich Stauffer (born on 6 February 1943) passed away on 6 August 2019. In addition to being an outstanding and internationally recognized scientist who made seminal contributions to multiple research fields, he was a long-time friend with a great heart, very funny, kind, always helpful to scientists from the third world and developing countries, and dedicated to the cause of peace. He will be sorely missed. The final version of this chapter was prepared by the Editor. Needless to say, any possible error or shortcoming of this chapter is entirely the Editor's fault

D. Stauffer: deceased.

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sites in the cluster. Because of this ambiguity, we discuss here mainly site percolation; bond percolation is similar in the sense that it belongs to the same universality class (the same critical exponents; see below). One may also combine both choices and study site-bond percolation where each site is randomly occupied or empty, and each bond between neighboring occupied sites is also randomly present or absent.

Neither temperature nor quantum effects enter this standard percolation model, which is purely a problem in geometrical probability theory. To understand why percolation works the way it does, however, it is helpful to understand thermal phase transitions as in, for example, the vapor-liquid critical point. If the magnetic applications is of interest, it is useful to recall that according to quantum mechanics some spins (atomic magnetic moments) have only two states, up or down. We will explain such physics aspects later in this chapter.

For small p , most of the occupied sites are isolated with cluster size of $s = 1$, coexisting with only few pairs, clusters of size $s = 2$, and triplets, $s = 3$. For large p , on the other hand, most of the occupied sites form one “infinite” cluster that spans the lattice from left to right (or between two opposite faces or surfaces), with a few small isolated holes (unoccupied sites) in it. Thus, there exists a critical value of p , called the percolation threshold p_c , such that for $p < p_c$ we have no spanning cluster, whereas for $p > p_c$ we have (at least) one spanning cluster. Despite decades of research on this seemingly simple problem, no exact value of p_c has been proven or even guessed for site percolation on the square lattice with nearest-neighbor bonds. We only know numerically that $p_c \simeq 0.5927462$. For site percolation on the triangular lattice or bond percolation on the square lattice, $p_c = 1/2$ *exactly*. Values of the percolation thresholds are given in Table 1 (Essam 1980; Stauffer and Aharony 1994; Sahimi 1994; Grimmett 1999; Flory 1941; Grassberger 2003). They are valid in the limit that $L \rightarrow \infty$, where L is the linear size of the lattice, such that in d dimensions they contain L^d sites. For small L , instead of a sharp transition at p_c one has a rounded changeover: with a very low probability, one chain of L occupied sites at $p = 1/L^{d-1}$ spans

Scaling Theory of Percolation Clusters, Table 1 Site and bond percolation thresholds for various lattices in d dimensions (Essam 1980; Stauffer and Aharony 1994; Sahimi 1994; Grimmett 1999; Flory 1941; Grassberger 2003)

Lattice	D	p_c (site)	p_c (bond)
Linear chain	1	1	1
Honeycomb	2	0.697043	$1 - 2 \sin(\pi/18)$
Square	2	0.592746	1/2
Triangular	2	1/2	$2 \sin(\pi/18)$
Diamond	3	0.4301	0.3893
Simple cubic	3	0.311608	0.248813
Body-center cubic (BCC)	3	0.245691	0.180287
Face-center cubic (FCC)	3	0.199236	0.120163
Hypercubic	4	0.196885	0.160131
Hypercubic	5	0.140797	0.118172
Hypercubic	6	0.109018	0.094202
Hypercubic	7	0.088951	0.078675

from one side to the opposite. In one dimension, a small chain can easily span if p is close to one, but for $L \rightarrow \infty$, the threshold approaches $p_c = 1$, since for smaller p , a hole (unoccupied sites) will appear about every $1/(1-p)$ sites and prevent any cluster from spanning.

Theoretical Methods and Computer Simulation

This section summarizes some of the methods employed to determine percolation properties, first by pencil and paper, and then with the help of computers for which Fortran programs are published in, e.g., Redner 1982, Stauffer and Jan 2000. More details on simulations are reviewed by R.M. Ziff elsewhere in this book.

Mean-Field Approximation

The Bethe lattice or Cayley tree neglects all cyclic links (closed loops) and, thus, allows derivation of an exact solution by paper and pencil. We begin from one central site, and let Z bonds emanate from it. At the end of each bond sits a neighbor. Then, from each of the neighbors, Z bonds

emanate again, one back to the central site and $(Z - 1)$ to new sites farther outward. They, in turn, lead again each to $(Z - 1)$ new sites, and so on. None of the newly added sites is the same as one of the already existing sites and, therefore, we can travel along the bonds only outwards or back but never in a loop. It is quite plausible that an infinite cluster of bond percolation is formed if each site leads to at least one more outward site along an existing bond, which means if $(Z - 1)p > 1$, which also holds for site percolation. Thus,

$$p_c = (Z - 1)^{-1}, \quad (1)$$

for both bond and site percolation.

In this way, Flory calculated the threshold and other percolation properties, although he did not use our terminology. We now recognize this as the *mean-field approximation*, in analogy with thermal phase transitions. In the mean-field approximation, the critical exponents that characterize the power-law behavior of the various percolation properties and are described below are either integers or simple fractions. The Erdős-Rényi random graphs also belong to this universality class, in which one connects in an assembly of N points each pair with a low probability $\propto 1/N$. The same universality class is obtained, i.e., the same critical exponents are valid, if we let the dimension d of hypercubic lattices approach infinity, or at least take on values above 6. Thus, $d = 6$ is called the *upper critical dimension* of percolation, i.e., the spatial dimension at which the critical exponents become identical with those obtained for the Bethe lattice or mean-field approximation. A disadvantage of the Bethe lattice is its lack of realism: If the length of the bonds is constant, then the exponential increase of the number of sites and bonds with increasing radius leads to an infinite density, which does not exist in reality.

Small Clusters

The probability of a site to be isolated in the square lattice, i.e., a cluster of size $s = 1$, is $n_1 = p(1 - p)^4$, since the site must be occupied and all its four neighbors be empty. Similarly, for pairs of occupied sites one has, is $n_2 = 2p^2(1 - p)^6$, since the pair

can be oriented horizontally or vertically, resulting in the factor 2. Similar, only more difficult, is the evaluation of the number of clusters n_s of s sites, with a maximum value of s usually between 10 and 20. The general formula is given by:

$$n_s = \sum_t g_{st} p^s (1 - p)^t, \quad (2)$$

where the perimeter t is the number of empty neighbors and g_{st} is the number of configurations – called *lattice animals* or *polyominoes* – of size s and perimeter t . The King's College group in London (led by J.W. Essam (1980) and M.F. Sykes) published these results in the 1970s. With series expansion technique, borrowed from near thermal critical phenomena, these polynomials allow estimation of not only p_c , but also many other quantities (see below) that diverge or vanish near p_c .

Leath's Cluster Growth Algorithm

Leath (1976) developed an algorithm for growing the percolation clusters, instead of the simple random method described earlier. In his method, one begins with one occupied site at the center of the lattice. Then, a cluster is grown by letting each empty neighbor of an already occupied cluster site decide once and for all whether it is occupied or empty. One needs to keep and update a list of perimeter sites of undecided neighbors. If the list becomes empty, the cluster growth is finished, and none of the boundaries of the lattice influences the cluster, as it did not reach the boundaries. If, on the other hand, the cluster reaches the lattice boundary, one stops the simulation as the grown cluster is spanning, from the center to one of the sides. Repeating the growth simulation multiple times, one can estimate p_c , as well as the cluster numbers. More precisely, the cluster statistics obtained in this way is not the number n_s of clusters of size s but rather sn_s since the original central site belongs to a larger cluster with higher probability than to a smaller one.

The Hoshen-Kopelman Algorithm

To go regularly through a large lattice, which may even be an experimentally observed structure to

be analyzed by computer, one can number consecutively each seemingly new cluster, and if no clusters merge later, then, one has a clear classification: All sites belonging to the first cluster have label 1, those in the second cluster have label 2, etc. Unfortunately, this does not work. It may turn out in the latter stages of the analysis that two clusters that at first seemed separate actually merge and form one cluster. This is shown in Fig. 1.

In the simple structure shown in Fig. 1, we already have several such label conflicts. The labels to the right come from going through the lattice like a typewriter, from left to right, and after each line to the lower line. When we reach the right neighbor of the 3 in the figure, we see that it is really part of the cluster with label 2. At the right neighbor of 4, we see that it belongs to cluster 1. The naive method would be going back to relabel all the 3s into 2, and all the 4s into 1. But, then, if we reach the site marked with x , we see that the entire structure is really one single cluster and, thus, all the sites with label 2 must be relabeled into 1. This is highly inefficient for large lattices and, therefore, not useful.

Instead, Hoshen and Kopelman (1976) gave each site labels $m = 1, 2, 3, \dots$ another index $n(m)$. The label $n(m)$ of the labels equals its argument, $n(m) = m$, if it is still a good “root label,” and it equals another number k if the cluster with initial label m turned out later to be part of an earlier cluster k . By iterating the command $m = n(m)$ until the new m is finally equal to $n(m)$, one finds the root label. Thus, for Fig. 1, we make the following assignments and reassignments to n : $n(1) = 1$, $n(2) = 2$, $n(3) = 3$, $n(3) = 2$, $n(4) = 4$, $n(4) = 1$, and $n(2) = 1$. Clusters are now characterized by the same root label for all their labels. An advantage of this method is that only one line of the square lattice,

* *	* *	1 1	2 2
	* * * *	1	3 ? 2
* * * * *		4 ? ? x ?	

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Fig. 1 Classification of sites according to the Hoshen–Kopelman algorithm

or one hyperplane of the d -dimensional lattice, needs to be stored at any time, besides the array $n(m)$, and that array can also be reduced in size by regular recycling of no longer used labels n , just as beer bottles can be recycled. Using this method and parallel computers, lattices with more than 13^{th} sites were simulated. Understanding the details of the algorithms and finding errors in them can, however, be very frustrating.

Sometimes one wishes to determine the cluster numbers for numerous values of p from 0 to 1. In that case, instead of starting a new analysis for each different p , one may also fill the lattice with new sites and make the proper labeling of the labels whenever a new site was added (Newman and Ziff 2000). Similarly, one can determine the properties of lattices with various sizes L by letting L grow one by one and relabeling the cluster after each growth step (Tiggemann 2006). Unfortunately, the two methods came long after most of the percolation properties were already studied quite well by standard Hoshen–Kopelman analysis.

Relation to Ising and Potts Models

The relation between percolation and thermal physics was useful for scientists working on the two problems: scaling theories for percolation could follow those for thermal physics developed 10 years earlier, while computer simulations for thermal physics could use the Leath and Hoshen–Kopelman algorithms of cluster analysis, which led to the Wolff (1989) and Swendsen–Wang (1987) methods, respectively, a decade later. A mathematical foundation is given by the Kasteleyn–Fortuin theorem (Kasteleyn and Fortuin 1969) for the partition function Z_q of the q -state Potts model at temperature T :

$$Z_q = \langle q^N \rangle, \quad (3)$$

where N is the total number, $\sum_s n_s$, of clusters for bond percolation at probability $1 = \exp[-2J/(k_B T)]$, $\langle \cdot \rangle$ indicates an average over the configurations at this probability, k_B is the Boltzmann’s constant, and $2J$ is the energy needed to break a bond between neighboring spins. Recall

that each site i of a lattice in the Potts model carries a variable $S_i = 1, 2, \dots, q$, and that the energy of a neighbor pair is $2J$ if the two variables agree and 0 otherwise.

The cases for which $q \geq 3$ are interesting and important, since for increasing q , a second-order phase transition with a continuous order parameter changes into a first-order phase transition with a jumping (discontinuous) order parameter, as T increases. The special limit, $q = 2$ is the spin $1/2$ Ising model. (The model's name should be pronounced EEsing, not EYEsing, because Ernst Ising was born in Cologne, Germany, and became the US citizen Ernest Ising only *after* publishing his theory in 1925 and surviving Nazi persecution in 1933–1944.) The limit $q \rightarrow 0$ corresponds to some tree structures with no cyclic links, as in Flory's percolation theory (Deng et al. 2007). Percolation, on the other hand, corresponds to the limit $q \rightarrow 1$ in the following sense: In the $q=1$ limit, the “free energy” in units of $k_B T$ is $\ln Z_q = \ln \langle \exp(N \ln q) \rangle \simeq \ln \langle \exp[(q-1)N] \rangle \simeq \ln(1 + (q-1)N) \simeq (q-1)N$. Thus, for q near unity, the thermal free energy divided by $(q-1)$ is simply the number of percolation clusters.

In this way, thermal physics and percolation are related, and the cluster numbers correspond to a free energy. In thermal physics, the negative of the derivative of the free energy with respect to a conjugate field represents the order parameter, e.g., a magnetic field and magnetization, and the field derivative of the order parameter is called the *susceptibility*. For liquid-gas equilibria, the order parameter is the volume or the density; the field is the pressure or the chemical potential; and the analog of the susceptibility is the compressibility. We should keep in mind that this yields Eq. (3), not its derivation, if we look at the percolation quantities of interest.

Formally, we may define for percolation a free energy F as a generating function of a ghost field h :

$$F(h) = \sum_s n_s \exp(-hs). \quad (4)$$

Then, its first derivative is $-\sum_s s n_s$, and the second one is $\sum_s s^2 n_s$, sums that appear in the following in the percolation probability P_∞ i.e., the order parameter of percolation, and the mean

cluster size, $S = \sum_s s^2 n_s / \sum_s s n_s$, which represents the susceptibility for percolation.

Percolation Quantities and Critical Exponents

The most basic percolation quantity is n_s , the number (per site) of clusters containing s sites, which often is an average over several realizations for the same occupation probability p in the same lattice. Several moments defined by:

$$M_k = \sum_s s^k n_s, \quad (5)$$

are used to define other quantities of interest. In such sums, the infinite (spanning) clusters are omitted. The following power laws are valid asymptotically in the limit of large lattice size L and for $p \rightarrow p_c$:

$$F = M_0 \propto |p - p_c|^{2-\alpha} + \dots, \quad (6)$$

$$P_\infty = p - M_1 \propto (p - p_c)^\beta, \quad (7)$$

$$S = \frac{M_2}{M_1} \propto |p - p_c|^{-\gamma}. \quad (8)$$

Here, F is the analog of the thermal free energy, with the $\dots$ representing analytic background terms whose derivatives are all finite. Since every occupied site must belong either to a finite or to an infinite cluster, $P_\infty = p - \sum_s s n_s$ is the fraction of the sites that belong to the infinite cluster and represents the probability that from a randomly selected site, one can walk to a lattice boundary along a path of occupied sites. It is, thus, called the percolation probability, but it must be distinguished from the probability p that a single site is occupied, as well as from the probability R , with $R(p < p_c) = 0$, and $R(p > p_c) = 1$, that there is a spanning cluster in the lattice.

The quantity S is traditionally called the mean cluster size. We follow this tradition, even though it is very bad, because there are many ways to define a mean cluster size, and polymer chemists have the much more precise notions of a number average M_1/M_0 , a weight-average M_2/M_1 , and a Z-average

M_3/M_2 for the mean cluster size, which they call degree of polymerization. Physicists arbitrarily call the weight-averaged s the mean cluster size S . Numerically, the exponent γ is determined more easily from the “susceptibility,” $\chi = M_2 \propto |p - p_c|^{-\gamma}$, since the denominator M_1 in Eq. (8) approaches very slowly its asymptotic limit of 1.

The radius R_s of a cluster is defined as the root mean-square distance r_i , $i = 1, 2, \dots, s$ of cluster sites from the center of mass r_c of the cluster (radius of gyration):

$$R_s^2 = \left\langle \frac{\sum_i (r_i - r_c)^2}{s} \right\rangle, \quad (9)$$

where the $\langle \cdot \rangle$ represents an average over all cluster configurations at probability p . The correlation length ξ is related to the Z average cluster radius through:

$$\xi^2 = \frac{\sum_s R_s^2 s^2 n_s}{\sum_s s^2 n_s} \propto |p - p_c|^\nu, \quad (10)$$

which defines another critical exponent, ν . Finally, right at p_c , the cluster numbers decay as:

$$n_s \propto s^{-(2+1/\delta)}, \quad (11)$$

where δ must be positive in order to have a finite density $\sum_s s n_s = p$.

The five critical exponents that have been defined so far are not independent of each other but are related in d dimensions through the following scaling relations,

$$2 - \alpha = \gamma + 2\beta = (\delta + 1)\beta = d\nu, \quad (12)$$

which are already known in thermal phase transition. The last equation involving d is not valid in mean-field theory, i.e., large d , but only for $d \leq 6$. The scaling relations (12) can be derived by assuming that

$$n_s = s^{-\tau} f[(p - p_c)s^\sigma], \quad (13)$$

where $\tau = 2 + 1/\delta$ and $1/\sigma = \beta\delta$. Equation (13) was first postulated for Ising model and then

successfully applied to percolation. Here, f is a suitable scaling function that approaches a Gaussian function only in the mean-field limit. For both thermal critical phenomena and percolation, *universality* asserts that the critical exponents are independent of many details and (for the Potts model) depend only on the dimensionality d and the number q of possible spin states. Since percolation corresponds to $q \rightarrow 1$, this implies that the exponents depend only on d . There are exceptions to this universality for thermal phase transitions, but for random percolation universality has so far held up. Note, however, that the numerical value of the percolation threshold p_c depends on the lattice structure and is different for site and bond percolation.

The universality of the critical exponents is one of many reasons why their investigation is important: They allow to classify models and materials. Similarly, in biology, we have many birds of different colors and many types of domestic animals. Biology became a systematic science only when it was found that all mammals share certain properties, which birds do not have. Thus, there is the “universality class” of mammals.

On the other hand, the proportionality factors in the above equations are not universal, but some of their combinations are. For example, the ratio of the proportionality factors for mean cluster size S above and below p_c is universal. In addition, in some sense the probability $R(p = p_c)$ of a lattice to contain one spanning cluster at the threshold is also universal, since it takes on the same value for both bond and site percolation. However, $R(p = p_c)$ depends on the boundary conditions and the shape of the sample and, thus, it universality is much weaker than the aforementioned ratio for S .

Table 2 presents the numerical estimates of the exponents in three dimensions, as well as their mean-field values for $d \geq 6$ and their exact values for 2D systems (Nienhuis 1982; Smirnov and Werner 2001). Thus, for six- and fewer-dimensional systems, knowledge of two of the exponents suffices for knowing the values of all of them.

Unfortunately, there is another exponent that is not related to the cluster numbers and radii, and

Scaling Theory of Percolation Clusters, Table 2 Critical exponents for percolation clusters. The mean-field values are valid for six and more dimensions, and are also applicable to Flory's Bethe approximation, as well as to Erdős-Rényi random graphs. Values of the exponents α , δ , σ , and τ can be obtained from the scaling relations, Eq. (12)

d	β	γ	N
2	5/36	43/18	4/3
3	0.41	1.796	0.88
≥ 6	1	1	$\frac{1}{2}$

for which no scaling relation has been found that relates it to the other exponents defined earlier. This refers to the electrical conductivity when each occupied site (or bond) conducts electrical current and each empty site (or deleted bond) is an insulator. Near p_c , the effective conductivity σ_e of the system follows the following power law,

$$\sigma_e \propto (p - p_c)^\mu, \quad (14)$$

which defines the exponent μ , whose numerical values are 1.30, 2.0, and 3 in two, three, and at least six dimensions. If the bonds represent elastic springs with bending forces, the elastic exponent may be $\mu + 2\nu$ (Sahimi 1986) if entropy effects are negligible, or $2 - \alpha = \nu d$ if such effects are dominant. Moreover, the universality of μ is not as strong as that of the geometrical exponents defined so far. The aforementioned lattice values do not hold for a continuum, such as conducting spheres with overlaps. Similarly, the kinetics of the Ising model determine a critical exponent that differs in different variants of the kinetics and may not be related to the static Ising exponents, such as β and γ . The conductivity and elasticity of percolation lattices are described and discussed in detail elsewhere in this book.

Fractal Dimensions of Percolation Clusters

In addition to the power laws and the associated critical exponents, percolation clusters are also characterized by various fractal dimensions, which are described next.

Self-Similarity and Fractal Dimension

Typical objects of geometry class in high school are one-dimensional lines, two-dimensional squares or circles, and three-dimensional cubes or spheres. They have a length (radius) L and a mass (volume for unit density) M with $M \propto L^d$ in d dimensions. In reality, mother Nature produces much more complex objects, such as trees, where the mass varies with a power of the tree height below 3:

$$M \propto L^D, \quad (15)$$

where $D < d$ is the fractal dimension, and the limit $L \rightarrow \infty$ is implied. Such objects are called *fractals*, particularly if they also are self-similar in that a small twig looks like a big branch, etc. Finite-size scaling theory relates D of the largest (sample-spanning) cluster at $p = p_c$ to the percolation exponents already introduced through

$$D = d - \frac{\beta}{\nu} = \frac{\gamma + \beta}{\nu} = \frac{1}{\sigma\nu} = \frac{d}{1 + 1/\delta}, \quad (16)$$

for $d \leq 6$. Thus, the critical percolation cluster is about 1.9-dimensional in two and 2.5-dimensional in three dimensions, whereas in the mean-field regime for $d \geq 6$, we have $D = 4$.

Why is this so? Any quantity X that is supposed to vary near $p = p_c$ as $|p - p_c|^x$ does so only for infinitely large systems. For a finite lattice size L , the percolation transition is rounded, and neither X nor any of its p derivatives diverges or vanishes exactly. In particular, the typical cluster radius or correlation length $\xi \propto |p - p_c|^{-\nu}$ cannot become infinite but becomes of the order of L . Then, the relation $X \propto \xi^{-x/\nu}$ is replaced by:

$$X(p = p_c) \propto L^{-x/\nu}, \quad (17)$$

and $X(p \simeq p_c) = L^{-x/\nu} g[(p - p_c)L^{1/\nu}]$ near the percolation threshold with a suitable scaling function $g(y)$. In particular, the fraction P_∞ of the sites belonging to the largest cluster at $p = p_c$ vanishes as $L^{-\beta/\nu}$ and the total number M of sites in this cluster as:

$$M \propto L^{d-\beta/\nu}, \quad (18)$$

or $D = d - \beta/\nu$, as asserted.

Figure 2 shows the second moment $\chi = M_2 = \sum_s s^2 n_s$ in small (curve) and large (+) simple cubic lattices, differing only for $p \simeq p_c$. Figure 3 presents right at $p = p_c$ the variation with the lattice size of the number M of the sites in the largest cluster and of the second moment M_2 , i.e., the susceptibility.

In a finite lattice, the probability $R(p)$ of a spanning cluster to exist increases from nearly zero to nearly unity in a p interval proportional to $1/L^{1/\nu}$, according to Eq. (17) with $x = 0$. The derivative dR/dp is the probability that spanning the lattice first occurs at probability p . It is plausible that this probability, peaked around p_c , is a Gaussian distribution. Unfortunately, the ruler of the Evil Empire [in the Department of Chemical Engineering at the University of Michigan] destroyed (Ziff 1994) this beautiful idea: Since for $p \simeq p_c$ and $\xi \sim L$, every part of the lattice is correlated with the rest of the lattice, the central limit theorem does not hold.

On the other hand, if for $p \ll p_c$, we let the cluster size s diverge, which requires a special algorithm, we obtain the universality class of *lattice animals*. Most simply, in the limit $p \rightarrow 0$, Eq. (2) simplifies to $n_s/p^s = g_{st}$, which means we look at the distribution of the configurations with s sites and perimeter t , where all the configurations

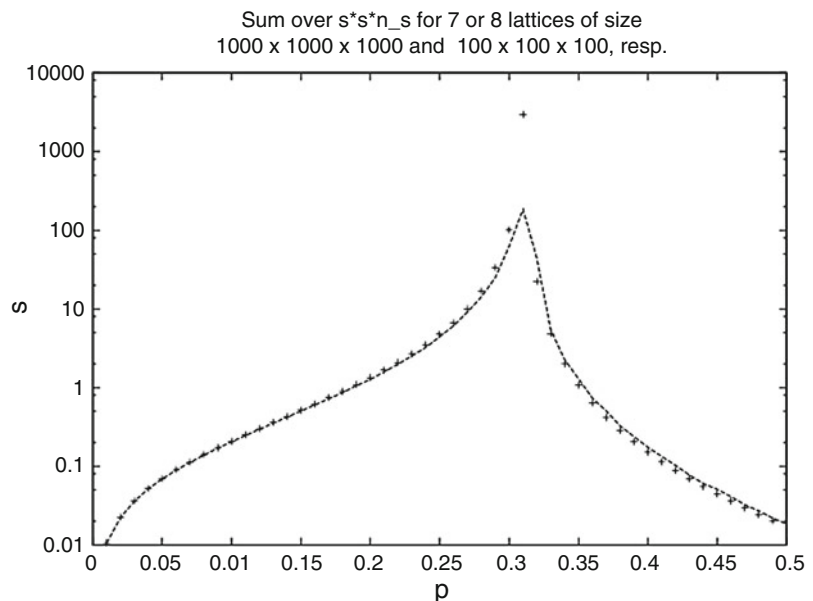
of a given s are weighted equally, regardless of what their perimeter t is. An important result for the animals is that in three dimensions, their radius R_s varies as $\sqrt{s}$, i.e., their fractal dimension is exactly 2. In two dimensions, only numerical estimates exist with $D \simeq 1.56$. It is highly unusual that a problem has an exact solution in three but not in two dimensions.

Incipient Infinite Cluster

Right at $p = p_c$, the largest cluster spans the lattice with a pseudo-universal probability $0 < R(p_c) < 1$ and then has a density P_∞ that vanishes for $L \rightarrow \infty$. The cluster is also called the *incipient infinite cluster* (IIC). Most of the IIC consists of dangling ends that carry no current if the cluster is interpreted as a random resistor network with conductivity σ_c ; see Eq. (14). The remaining current-carrying part of the cluster is called the *backbone* that has a fractal dimension of 1.643 in two dimensions, 1.9 in three, and 2 in at least six dimensions, and consists mostly of blobs where current flows along several parallel, though connected, paths. The few *articulation* sites or bonds, the removal of which cuts the network into two or more parts, are called the *red bonds*

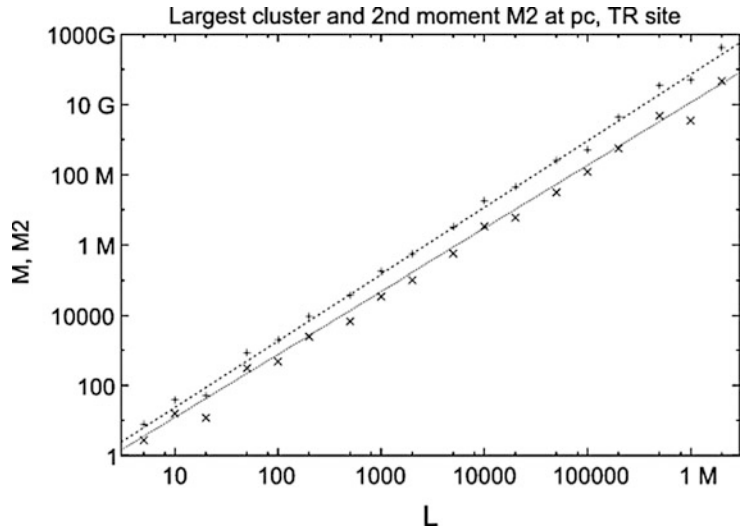
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Fig. 2 Susceptibility M_2 in the simple-cubic lattice. For the smaller size, the maximum is reduced appreciably



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Fig. 3 Number M of sites in the largest cluster (+) and the susceptibility M_2 (x) at $p = p_c = 1/2$ for triangular site percolation. The two straight lines have the exact slopes $D = 91/48$ and $\gamma/\nu = 43/24$, predicted by finite-size scaling. The largest lattice took about 36 h on a workstation with 2Gb memory to simulate. Tiggemann (2006) simulated $L = 7 \times 10^6$, 25024, 1305, 225 for $d = 2, 3, 4$, and 5 on a large parallel computer



since all the current flows through them (and, thus, they “heat up” and become red), and have a fractal dimension of only $1/\nu = 3/4$, 1.14, and 2 in two, three, and six dimensions or larger.

How many infinite clusters exist? The easy answer is none below p_c ; perhaps one at p_c , and always one above p_c in an infinite lattice. Indeed, this is what was claimed mathematically in the 1980s (Newman and Schulman 1981): The number of infinite clusters is zero, one, or infinite. Later, mathematical analysis excluded the last choice, infinitely many clusters, even though in seven dimensions scaling arguments, confirmed by numerical studies (de Arcangelis 1987), indicated the number of the IIC diverge for increasing L . Only in 1995 and later Aizenman (1997) predicted that in all dimensions, one may have several spanning clusters at $p = p_c$, in agreement with simulations (Shchur and Rostunov 2002).

Why were the earlier uniqueness theorems irreproducible at p_c and for very elongated rectangles even above p_c (Stauffer 1999)? A clear definition of “infinite” is missing in some of the mathematics, although Newman and Schulman (1981) defined a cluster as infinite if its cardinality, i.e., the number of sites in it, is infinite for $L \rightarrow \infty$ in a hypercubic lattice of L^d sites. Clear definitions of infinity are, of course, needed for reliable proofs (Jarai 2003). Measure theory, as applied in some theorems, may be based on some axioms that are not applicable for

a fractal IIC. Very simply, imagine each line of an $L \times L$ square lattice to have one randomly selected site occupied and all others empty. The set of occupied site then has cardinality L , which is infinite for infinite lattices, but its density is zero. Does the measure theory agree with this? More relevant for percolation, even for $p < p_c$, is that the largest cluster has a size increasing logarithmically with lattice size and, thus, can be described as infinite, invalidating the percolation threshold as the onset of infinite clusters. Thus, infinite might be defined as increasing with a positive power of L , i.e., having a positive fractal dimension. Then, we have infinitely many infinite clusters only at $p = p_c$, though in most cases, only the largest of them is a spanning cluster. Using spanning as a definition of an infinite cluster seems to cause the smallest problems.

Thus, one should not regard a question as settled if some mathematical theorem claims to have answered it. The mathematics may not apply to the same problem one is interested in, or – see bootstrap percolation in this book – may apply only for unrealistically large lattices. On the other hand, computer simulations should also be relied upon only if confirmed independently. Moreover, in the interpretation of simulation results, one should be objective and not try to agree with prevailing theories. For example, de Arcangelis (1987) might already have seen the multiplicity of

infinite clusters in five dimensions, not just in seven dimensions, had she not followed her obviously “incompetent” postdoctoral mentor [whom we do not name]! On a more positive side, mathematicians (Berger et al. 2003) solved the problem of biased diffusion on percolating clusters above p_c only a few years after physicists still had controversies about their simulations.

Simple Renormalization Group Transformations

Why are scaling laws and finite-size scaling so simple? Why are the critical exponents universal? Such question arose for thermal critical phenomena, as well as for percolation. The main reason is that the correlation length ξ diverges at the critical point. Thus, all approximations that restrict the correlations to some finite lengths eventually break down and, instead, the scaling ideas become correct. They were explained by Ken Wilson through what he called renormalization group theory around 1970, for which he received the physics Nobel prize in 1982. Basically, since the correlations extend over long distances, the single atom or lattice point becomes irrelevant and can be averaged over. In politics, we have a similar effect: Many democracies are based on electoral districts, and the candidate winning most votes within his/her district represents it in the national parliament. It is the cooperation of many people within the electoral district, not the single vote, which is decisive.

Returning to a $L \times L$ lattice, we can divide it into many blocks of linear dimension b and treat a block analogously to an electoral district. Thus, in the Ising model, if the majority of block spins point upward, then the entire block is represented by a superspin pointing up, analogous to the single representative in politics. These block spins then act like the original spins, one can put $b \times b$ superspins into one superblock and have just one super-representative following the majority opinion of the representatives within the superblock. This process can be continued: at each stage $b \times b$ the lower representatives are normalized into a single higher representative.

Such a renormalization by majority rule works fine with Ising spins, but percolation deals with connections, not with up and down spins. Thus, for percolation, a $b \times b$ block is normalized into an occupied supersite, if and only if there is a spanning cluster within the block; otherwise, the superblock is considered empty. In this way, entire blocks are normalized into single sites via connectedness. Then, the renormalization process is reduced to the standard question that was already asked before Wilson's work: Does a $b \times b$ lattice have a spanning cluster? The supersite is thus occupied if and only if the block spans, which happens with probability $R_b(p)$. If p' is the probability of the supersite to be occupied, we must have:

$$p' = R_b(p). \quad (19)$$

If the lattice is at $p = p_c$, then the renormalization transformation should not change anything drastic since the correlation length ξ is larger than any b . Thus, if the renormalization could be exact, we would have:

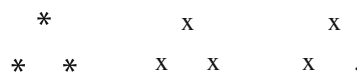
$$p'_c = R_b(p_c). \quad (20)$$

Practically speaking, we determine a *fixed point* $p = p^*$ such that:

$$p^* = R_b(p^*), \quad (21)$$

and, then, determine p_c as the limit of p^* for $b \rightarrow \infty$, which again is similar to what percolation experts did before the renormalization theory.

A particularly simple example is the triangular site percolation problem with $p_c = 1/2$, if we do not divide the lattice into large $b \times b$ blocks, but into small triangles of three sites that are nearest neighbors, as shown on the left side of Fig. 4:



Scaling Theory of Percolation Clusters, Fig. 4 (Left) The basic cell in the triangular network. (Right) the configurations of the site in the basic cell that can be occupied (x)

The triangle contains a spanning cluster if either all the three sites are occupied (x in the central diagram) or two sites are occupied (x) and one site is empty (·, the right diagram). The first choice appears with probability p^3 and the second with probability $p^2(1-p)$. The second choice has, however, three possible orientations since each of the three sites can be the single empty site. Thus, the total probability of the triangle to have a spanning cluster is:

$$p' = p^3 + 3(1-p)p^2, \quad (22)$$

with three fixed points p^* where $p' = p_c$, namely, $p^* = 0, 1/2$, and 1. The second of the three fixed points is the *exact* percolation threshold, while the first corresponds to lattice animals, discussed earlier in the sections on small clusters and fractal dimension, while the third fixed point represents compact non-fractal clusters. With somewhat more effort, one can derive also a good approximation for ν , the critical exponent of the correlation length. The agreement between the fixed point p^* with the exact threshold $p_c = 1/2$ does not hold for other lattices or block choices. Nevertheless, there was a widespread fixed-point consensus that $R_b(p_c) = p_c$ for sufficiently large b .

Regrettably, the aforementioned ruler of the Evil Empire destroyed this beauty too (Ziff 1992) and obtained $R_b(p_c) = 1/2$ for square site percolation whereas $p_c \simeq 0.593$. As mentioned earlier, in general, $R(p_c)$ is a pseudo-universal quantity that depends on the boundary conditions and sample shape, whereas p_c for large lattices is independent of such details but is different for site and bond percolation and depends on the coordination number Z , the number of neighboring sites. Thus, life was much nicer before the “destructive” work of the Evil Empire. Fortunately, if a fixed point is determined by $p^* = R_b(p^*)$, and the block size b becomes very large, then, the fixed point will still approach the true p_c . In fact, it was shown (Sahimi and Rassamdana 1995) that equation $R_b(p^*) = \alpha$ with *any* $0 < \alpha \leq 1$ always yields an estimate of p_c that becomes more accurate as b increases.

Twenty years ago, it was claimed that percolation, as a research field, is dead, similar to Fortran

programming. Not so! It is alive and kicking. But, the author believes, nevertheless, that the future is more in the applications of percolation, including to social percolation (Weisbuch and Solomon 2002) for marketing by word-of-mouth, stock market fluctuations due to herding among traders (Cont and Bouchaud 2000), percolation in cell physiology (Aon et al. 2004), signals within a bacterial community (Larkin et al. 2018), and biological evolution (Katsnelson et al. 2019).

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Correlated Percolation

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Definition of the Subject and Its Importance

Cluster concepts have been extremely useful in elucidating many problems in physics. Percolation theory (Grimmett 1989; Stauffer and Aharony 1994; Sahimi 1994) provides a generic framework to study the behavior of the cluster distribution. In most cases the theory predicts a geometrical transition at the percolation threshold, characterized in the percolative phase by the presence of a spanning cluster, which becomes infinite in the thermodynamic limit. Standard percolation usually deals with the problem when the constitutive elements of the clusters are randomly distributed. However, correlations cannot always be neglected. In this case correlated percolation is the appropriate theory to study such systems. The origin of correlated percolation could be dated back to 1937 when Mayer (Mayer 1937;

Mayer and Ackermann 1937; Mayer and Harrison 1938; Mayer and Mayer 1940) proposed a theory to describe the condensation from a gas to a liquid in terms of mathematical clusters (for a review of cluster theory in simple fluids see Sator (2003)). The location for the divergence of the size of these clusters was interpreted as the condensation transition from a gas to a liquid. One of the major drawbacks of the theory was that the cluster number for some values of thermodynamic parameters could become negative. As a consequence, the clusters did not have any physical interpretation (Fisher 1967a, b, 1971; Fisher and Widom 1969). This theory was followed by Frenkel’s phenomenological model (Frenkel 1939a, b), in which the fluid was considered as made of non-interacting physical clusters with a given free energy. This model was later improved by Fisher (1967a), who proposed a different free energy for the clusters, often called droplets, and consequently a different scaling form for the droplet size distribution. This distribution, which depends on two geometrical parameters, σ and τ , has the nice feature that the mean droplet size exhibits a divergence at the liquid-gas critical point. Interestingly, the critical exponents of the liquid gas critical point can be expressed in terms of the two parameters, σ and τ , and are found to satisfy the standard scaling relations proposed at that time in the theory of critical phenomena.

Introduction

Fisher’s droplet model was very successful, to describe the behavior of a fluid or of a ferromagnet near the critical point, in terms of geometrical cluster. However, the microscopic definition of such a cluster, in a fluid or ferromagnet was still a challenge. While the exact definition in a continuum fluid model is still an open problem, a proper definition in the Ising model or lattice gas model has been provided. A first attempt to define a cluster in the Ising model, which had the same properties of Fisher’s droplet model, was to

consider a cluster as set of parallel spins. In two dimensions indeed these clusters seemed to have the properties of Fisher's droplets, i.e., the mean cluster size of these clusters was found to diverge at the Ising critical point on the basis of numerical analysis (Binder 1976). This result was later proved rigorously (Coniglio et al. 1976). However, the critical exponents for the mean cluster size in $2d$ was found to be larger than the corresponding critical exponent of the susceptibility (Sykes and Gaunt 1976), contrary to the requirement of Fisher's droplet model. Moreover, numerical simulations in $3d$ and analytical result on the Bethe lattice showed that the critical point and the percolation point of such clusters were different. It was clear then that the clusters made of nearest neighbors parallel spins were too big to describe correlated regions. It was then proposed (Coniglio and Klein 1980) a different definition of clusters obtained by breaking the clusters of parallel spins by introducing fictitious bonds with a probability p_b between parallel spins. The new clusters are defined as a maximal set of parallel spins connected by bonds. For a particular choice of $p_b \equiv p = 1 - e^{-2J/k_B T}$ it was shown that these clusters (Coniglio-Klein droplets) have the same properties of Fisher's droplets, namely, their size diverges at the Ising critical point with Ising exponents. Note that the bonds are only fictitious and do not change the energy of the spins. They only have the role of breaking the clusters made of parallel spins. Some years earlier, Fortuin and Kasteleyn defined a random cluster model, obtained starting from an Ising model and by changing the spin interaction J in $J = \infty$, with probability p , and J into $J = 0$, with probability $1 - p$. They showed that the partition function of this modified model, called random cluster model, coincides with the partition function of the original Ising model. In the random cluster model, the clusters are defined as maximal set of spins connected by infinite interactions. Although these clusters have the same properties of the droplet model, they were defined in the random cluster model, and for this reason these clusters were not associated to the droplets of the Ising model. It was only after Swendsen and Wang (1987) introduced a cluster dynamics based on the Coniglio-Klein (CK) and Fortuin and Kasteleyn (FK) formalism, that it was formally shown (Coniglio et al. 1989) that the distribution of the CK droplets are the same as the

distribution of FK clusters in the random cluster model. For this reason, often the CK droplets and the FK clusters are identified; however, the different meaning should be kept in mind.

A further development was obtained when the fractal structure of the droplets was studied not only for the Ising model but for the full hierarchy of the q -state Potts model, which in the limit $q = 1$ gives the random percolation problem. It was shown that the critical droplets of the Potts model have the same structure, made of links and blobs, as found for the clusters in the random percolation problem. One of the consequences of this study was a better understanding of scaling and universality in terms of geometrical cluster and fractal dimension (Mandelbrot 1982).

The cluster approach to the phase transitions lead also to a deeper understanding of why critical exponents do not depend on dimensionality above the upper critical dimension, and coincide with mean field exponents. It was indeed suggested (Coniglio 1985) that, at least for random percolation, the mean field behavior is due to the presence of an infinite multiplicity of critical clusters at the percolation point. This suggests that similar results may be also extended to thermal problems.

Although the original interest in the field of correlated percolation was the study of critical phenomena in terms of geometrical concepts, later it was suggested that correlated percolation could be applied to the sol-gel transition (Coniglio et al. 1979, 1982), in particular when correlation was too large to be neglected. In many cases indeed the sol-gel transition, which is based on long-range connectivity and percolation transition, interferes with large-density fluctuation or critical point. The interplay between percolation points and critical points gives rise to interesting phenomena which are well understood within the concepts of correlated percolation. Correlated percolation has been studied also in systems with different types of long-range correlation (Weinrib 1984; Weinrib and Halperin 1983; Sahimi and Mukhopadhyay 1996; Sahimi et al. 2000; Makse et al. 1996) and has been applied to many other fields such as nuclear physics (Ma 1999, Ma et al. 2004), Gauge Theory (Fortunato and Satz 2000a, b) and $O(n)$ models (Bialas et al. 2000; Blanchard et al. 2000), fragmentation (Campi and Krivine 2005; Campi et al. 2003;

Mader et al. 2003), urban growth (Makse et al. 1998, 1995), random resistor network (Bastiaansen and Knops 1997), interacting colloids (Bug et al. 1985; Safran et al. 1985), and biological models (Abete et al. 2004).

In section “Random Percolation,” we introduce random percolation concepts. In section “Percolation in the Ising Model,” the context of the Ising model is shown: how clusters have to be defined in order to describe correlated regions corresponding to spin fluctuations. In sections “Ising Clusters” and “Ising Droplets” the Ising clusters and droplets are, respectively, introduced, and in section “Droplets above $d = 4$ ” it is shown how the mapping between thermal properties and connectivity breaks down below T_c above $d = 4$. In section “Generalization to the q -state Potts Model,” the results found for the Ising model are extended to the q -state Potts model, and in section “Fractal Structure in the Potts Model: Links and Blobs,” the fractal structure is studied in terms of links and blobs. In section “Fortuin Kasteleyn-Random Cluster Model” the FK Random Cluster Model is presented, and the connection with the CK droplets is further developed in Appendix. In section “Hill’s Clusters,” the possibility to extend the definition of droplets to simple fluids is discussed. In section “Clusters in Weak and Strong Gels,” the mechanism, leading to the formation of bound states in gelling systems, is considered, and in section “Scaling Behavior of the Viscosity,” the effect that finite bond lifetime has on the behavior of viscosity in weak or colloidal gels. Finally, future directions and open problems are discussed in section “Future Directions.”

Random Percolation

In this section we define some connectivity quantities and present some results in the context of random percolation, which we will use in the following sections, where the correlated percolation will be presented.

Consider a d -dimensional hypercubic lattice of linear dimension L . Suppose that each edge has a probability p of being occupied by a bond. For small values of p , small clusters made of sites connected by nearest-neighbor bonds are formed.

Each cluster is characterized by its size or mass s , the number of sites in the cluster. For large values of p in addition to small clusters we expect a macroscopic cluster that connects the opposite boundaries. This spanning cluster becomes infinite as the system size becomes infinite. For an infinite system there exists a percolation threshold p_c below which only finite clusters are present. At p_c the spanning cluster is usually called the incipient infinite cluster (IIC).

In order to describe the percolation transition (Essam 1980; Stauffer and Aharony 1994; Bunde and Havlin 1991; Havlin and Bunde 1991), one defines: an order parameter, $P_\infty(p)$, as the density of sites in the infinite cluster, the mean cluster size, $S(p)$, of the finite clusters, and the average number of clusters, $K(p)$.

These quantities can be related to the average number of clusters of s sites per site, $n(s, p)$, and near the percolation threshold the critical behavior is characterized by critical exponents:

$$K(p) \Big|_{\text{sing}} = \sum n(s, p) \Big|_{\text{sing}} \sim |p - p_c|^{2-\alpha_p}, \quad (1)$$

$$P_\infty(p) = 1 - \sum s n(s, p) \sim \begin{cases} 0 & \text{if } p < p_c \\ (p - p_c)^{\beta_p} & \text{if } p > p_c, \end{cases} \quad (2)$$

$$S(p) = \sum s^2 n(s, p) \sim |p - p_c|^{-\gamma_p}, \quad (3)$$

where the sum is over all finite clusters, and in Eq. (1) only the singular part has been considered.

Finally, one can define the pair connectedness function p_{ij}^f as the probability that i and j are in the same finite cluster. This quantity, which plays the same role as the pair correlation function in a second-order phase transition, close to the critical point behaves as:

$$p_{ij}^f \sim \frac{g(r/\xi)}{r^{d-2+\eta_p}} \quad (4)$$

where $r = |r_i - r_j|$, $g(x)$ is a rapidly decreasing function of x and ξ is the connectedness length corresponding to the diameter of the critical clusters, which diverges as

$$\xi \sim |p - p_c|^{-\nu_p}. \quad (5)$$

It can be shown that the pair connectedness function p_{ij}^f and the mean cluster size S satisfy the following relation (Essam 1980; Stauffer and Aharony 1994)

$$S = \sum_i p_{ij}^f \quad (6)$$

The critical exponents defined in Eqs. (1, 2, 3, 4, and 5) are not all independent. Scaling relations can be derived among them as for ordinary second-order phase transitions. An immediate relation follows from Eqs. (3), (4), (5), and (6)

$$\gamma_p/\nu_p = 2 - \eta_p \quad (7)$$

This and other scaling laws, as we will see, are intimately related to the fractal properties of the IIC (Mandelbrot 1982). The mass s^* , i.e., the number of sites in a typical cluster of linear dimension ξ , scales as $s^* \sim \xi^{D_p}$, where D_p is the fractal dimension of the cluster.

Scaling and Hyperscaling

In this section, we derive standard scaling laws, following Kadanoff's original idea. To fix the ideas consider to be just below the percolation threshold. We perform (Coniglio 1985) the following three steps: (i) divide the system into cells of linear dimension b , (ii) coarse grain by some suitable rule, and (iii) rescale the lengths by a factor b . The result is renormalized system where the size of the large clusters s has been reduced by factor b^{D_p} and all lengths by a factor b :

$$L' = L/b, \xi = \xi'/b, s' = s/b^{D_p}. \quad (8)$$

Assuming that the large clusters do not interpenetrate, the sum over the large clusters in an interval between $(s, s + \Delta s)$ must be the same before and after rescaling, i.e.,

$$N(s, \xi) \Delta s \sim N(s', \xi') \Delta s' \quad (9)$$

where $N(s, \xi)$ is the total number of clusters of size s . Dividing Eq. (9) by the volume L^d , from Eq. (8) we obtain

$$\bar{n}(s, \xi) = b^{-d-D_p} \bar{n}(sb^{-D_p}, \xi b^{-1}). \quad (10)$$

where $\bar{n}(s, \xi) = N(s, \xi)/L^d = n(s, p)$. Choosing $b = s^{1/D_p}$ from (10) we obtain

$$n(s, p) = s^{-\tau_p} f((p - p_c) s^{\sigma_p}) \quad (11)$$

with

$$\tau_p = \frac{d}{D_p} + 1 \quad \sigma_p = \frac{1}{\nu_p D_p}. \quad (12)$$

Eq. (11) exhibits the scaling form postulated by Stauffer (Stauffer and Aharony 1994; Bunde and Havlin 1991; Havlin and Bunde 1991). From (1), (2), and (12) we have:

$$\begin{aligned} 2 - \alpha_p &= \frac{\tau_p - 1}{\sigma_p}, \beta_p = \frac{\tau_p - 2}{\sigma_p}, -\gamma_p \\ &= \frac{\tau_p - 3}{\sigma_p} \end{aligned} \quad (13)$$

and

$$\tau_p = 2 + \frac{\beta_p}{\beta_p + \gamma_p}, \sigma_p = \frac{1}{\beta_p + \gamma_p}, \quad (14)$$

from which the following scaling relation are obtained:

$$\alpha_p + 2\beta_p + \gamma_p = 2, \quad (15)$$

$$\frac{1}{\nu_p} (\beta_p + \gamma_p) = D_p. \quad (16)$$

From (7, 12, 13), one can also find relations, which contain the Euclidean dimensionality, d , called hyperscaling relation:

$$2 - \alpha_p = v_p d, \quad (17)$$

$$d - \frac{\beta_p}{v_p} = D_p, \quad (18)$$

$$\eta_p = 2 + d - 2D_p. \quad (19)$$

Eq. (18) was originally suggested in Kirkpatrick (1978). In $2d$ exact results give $\tau_p = 187/91$ and $\sigma_p = 36/91$, and in $3d$ the best estimates $\tau_p \simeq 2.18$, $\sigma_p \simeq 0.45$. From mean field theory (Harris et al. 1975) we know that for any d above the upper critical dimension $d_c = 6$, the critical exponents coincide with the Bethe lattice solution, namely, $-\alpha_p = \beta_p = \gamma_p = 1$, $v_p = \sigma_p = 1/2$, $\eta_p = 0$ and $\tau_p = 5/2$. These exponents satisfy the scaling relation (15), but fail to satisfy the hyperscaling relation (17) except for $d = 6$.

Moreover, while Eq. (16), for any $d > 6$, shows that the fractal dimension is stacked at the value $D_p = 4$, the hyperscaling relation (18) breaks down for $d > 6$.

Breakdown of Hyperscaling

Breakdown of hyperscaling in critical phenomena is usually attributed to the presence of dangerous irrelevant variables (Fisher 1983). This approach based on dangerous irrelevant variables was developed in the particular case of percolation by Aharony, Gefen, and Kapitulnik (Aharony et al. 1984). We follow here a less conventional scaling approach, where a geometrical interpretation of hyperscaling, and why it breaks down above $d_c = 6$, was proposed (Coniglio 1985, 2000). Let us assume that the singular behavior comes only from the critical clusters. Say N_ξ the number of such clusters in a volume of the order ξ^d . The singular part of the cluster number is given by

$$\frac{N_\xi}{\xi^d} \sim \xi^{\frac{2p-2}{v_p}}. \quad (20)$$

At the same time, the density of sites in the infinite cluster $P_\infty \sim |p - p_c|^{\beta_p}$ scales as the total mass of the spanning clusters $N_\xi s^*$ in a volume of

linear dimension ξ divided by the volume ξ^d , namely

$$\frac{N_\xi \xi^{D_p}}{\xi^d} \sim \xi^{-\beta_p/v_p}, \quad (21)$$

where we have used $s^* \sim \xi^{D_p}$. Similarly, the mean cluster size:

$$\frac{N_\xi \xi^{2D_p}}{\xi^d} \sim \xi^{2\gamma_p/v_p}. \quad (22)$$

From these equations one gets the scaling relations, Eqs. (15) and (16). For example, from Eqs. (21) and (22) one easily obtains Eq. (16). If N_ξ is not a critical quantity, being a finite constant at the threshold, from these equations we recover also the hyperscaling relations. For example, from Eq. (20) follows the hyperscaling relation (17) and from Eq. (21) follows the hyperscaling relation Eq. (18). Otherwise if N_ξ diverges, hyperscaling breaks down. We know that for dimension d above $d_c = 6$, from the Bethe lattice solution (Fisher and Essam 1961) $n(s, p) \sim s^{-5/2} e^{-(p-p_c)^2 s}$ for large s . Therefore $N_\xi = \xi^d \sum n(s, p) \sim \xi^{d-6}$, where $\xi \sim |p - p_c|^{-1/2}$. This calculation shows that, for $d > 6$, N_ξ diverges and hyperscaling breaks down, and from Eqs. (20) and (21), the hyperscaling relations are replaced by $2 - \alpha_p = 6v_p$ and $D_p = 6 - \beta_p/v_p$, which indeed are satisfied for mean field exponents.

Note that the standard scaling approach of previous section, which lead to both scaling and hyperscaling relations, assumed no relevant interpenetration of critical clusters. When as for $d > 6$ the number of critical clusters in a region of linear dimension ξ , N_ξ diverges as ξ^{6-d} , the scaling approach must be modified, taking into account that the renormalized number of clusters must be reduced by a factor b^{6-d} . Then Eq. (9) will be modified as $N(s, \xi)\Delta s = b^{6-d}N(s', \xi')\Delta s'$ which still leads to all the Eqs. (9), (10), (11), (12), (13), (14), (15), and (16), except that d is replaced everywhere by 6. In particular, both Eqs. (16) and (18) give a fractal dimension $D_p = 4$.

The multiplicity of infinite clusters above d_c was numerically shown in (de Arcangelis 1987; Fortunato et al. 2004). The average (finite) number N_ξ of distinct clusters below d_c have been estimated theoretically and calculated numerically (Aizenman 1997; Hu and Lin 1996; Stauffer 1997). In conclusion, for $d > 6$, in a region of linear dimension ξ , there are $N_\xi \xi^d \sim \xi^{d-6}$ critical clusters of mass $M \sim \xi^4$ with fractal dimension $D_p = 4$, which does not change with the dimensionality. However, the total mass $M_{tot} = N_\xi \xi^4 \sim \xi^{d-2}$ (below $d_c = 6$ $N_\xi \sim 1$, $M = M_{tot} \sim \xi^{D_p}$). It is this proliferation of critical clusters which is responsible for the hyperscaling breakdown. As a consequence the critical clusters are separated by a new length ξ_1 given by $N_\xi \xi_1^d \sim \xi^d$ from which $\xi_1 \sim \xi^{6/d}$.

In conclusion, while for $d < 6$ the density of the order parameter fluctuates over a distance of the order ξ , for $d > 6$, where mean field holds, the fluctuations are damped by the presence of infinitely many interpenetrating clusters.

The mean field solution is therefore a consequence of the presence of infinitely many interpenetrating clusters which suppress the spatial fluctuation of the order parameter. Using this approach, we can obtain condition for the validity of mean field theory by imposing $N_\xi \gg 1$. Using Eqs. (21) and (16) this condition implies

$$N_\xi^{-1} \sim \frac{\xi^{v_p/v_p}}{\xi^d \xi^{-2\beta_p/v_p}} \sim \frac{\langle \Delta M^2 \rangle}{\xi^d M^2} \ll 1, \quad (23)$$

where M and $\langle \Delta M^2 \rangle$ are the order parameter and the fluctuations of the order parameter (here we used that the mean cluster size $S(p)$ has the same critical behavior as the fluctuations of the order parameter (Coniglio and Stauffer 1980; Chayes et al. 1989)). Interestingly enough Eq. (23) coincides with Ginzburg criterion for the validity of mean field theory.

The question of hyperscaling breakdown and its connection with the proliferation of infinite incipient clusters has been the subject of intense research. The problem is not as easy as it may seem. For example, one would predict that at p_c the number of disconnected incipient infinite clusters would behave as

L^{d-6} . It has been proven that this is the case (Aizenman 1997) if bulk boundary conditions are considered, namely, that clusters inside a box of linear dimension L can be connected also through sites in a larger domain containing the box. The same scaling behavior is expected also with free boundary conditions. Different results one expects instead if periodic boundary conditions are considered (Aizenman 1997; Fortunato et al. 2004; Kenna and Berche 2017), see in particular (Kenna and Berche 2017) for a general approach to all these different type of scaling.

Cluster Structure

Nodes and Links. In the previous sections we have shown that the IIC is a fractal.

Here we want to show in more details the internal structure of the IIC. A very useful nodes and links picture for the infinite cluster just above p_c was introduced by Skal and Shklovskii (1975) and de Gennes (1976). In this picture, the infinite cluster consists of a superlattice made of nodes, separated by a distance of the order of ξ , connected by macrobonds. Just below p_c the structure of the very large cluster, the IIC, was expected to have the same structure as the macrobonds.

Later on, in 1977, Stanley (1977) made the important observation that in general for each configuration of bonds at p_c the IIC bonds can be partitioned in three categories. By associating an electric unit resistance to each bond, and applying a voltage between the ends of the cluster, one distinguishes the dangling bonds, which do not carry current. The remaining bonds are the backbone bonds. The backbone can be partitioned in singly connected bonds (red bonds) and all the others, the multiply connected bonds, which lump together in “blobs.” The red bonds, which carry the whole current, have also the property that if one is cut the cluster breaks in two parts. Moreover, it was conjectured that (Stanley 1977; Stanley et al. 1976) the backbone could be represented by a self avoiding walk chain. This self avoiding walk Ansatz received a large amount of attention, since it predicted a value for the crossover exponent of the dilute Heisenberg ferromagnetic model near the percolation threshold in $2d$, not far from the $2d$ experimental data of

Birgeneau and coworkers on diluted Heisenberg ferromagnets (Birgeneau et al. 1976, 1980; Cowley et al. 1977a).

Sierpinsky gasket: a model without links. In 1981, a completely alternative model was proposed in Gefen et al. (1981). Based on the observation that in a computer simulation the red bonds were hardly seen, they proposed an alternative model, the Sierpinsky gasket, that represents the opposite extreme of the nodes and links picture. It has a self-similar structure but only multiply connected bonds are present. A great advantage of this model is that it can be solved exactly. It also gives good prediction for the fractal dimension of the backbone.

Nodes, links, and blobs. Motivated by all these conflicting models and by some puzzling experimental data on diluted ferromagnets, a theory was elaborated based on exact results. This theory led unambiguously to the formulation of nodes, links and blobs picture of the infinite cluster (Coniglio 1981, 1982), in which both links and blobs are relevant for $d < 6$, while blobs are irrelevant for $d \geq 6$. In particular the following relation was proven for any p and for any lattice in any dimension:

$$p \frac{dp_{ij}}{dp} = \lambda_{ij} \quad (24)$$

where p_{ij} is the probability that i and j are connected, λ_{ij} is the average number of red bonds between i and j , such that if one is cut, i and j would have been disconnected. From Eq. (24) it is possible to calculate the average number L_{ij} of red bonds between i and j under the condition that i and j are in the same cluster:

$$L_{ij} = \lambda_{ij}/p_{ij}. \quad (25)$$

From the scaling form of $p_{ij} = r_{ij}^{-d+2-\eta_p} f(r_{ij}/\xi)$ it follows

$$L_{ij} = r_{ij}^{1/v_p} f_1(r_{ij}/\xi), \quad (26)$$

where $f_1(x)$ is related via Eqs. (24) and (25) to $f(x)$ and goes to a constant for $x \ll 1$. In particular, by putting $r_{ij} = \xi$ in Eq. (26), we obtain

$$L_R \sim \xi^{1/v_p}, \quad (27)$$

where $L_R \equiv L(r_{ij} = \xi)$ is the average number of red bonds between two points separated by a distance of the order of ξ . From Eq. (27), it follows that the fractal dimension of the red bonds is $D_R = 1/v_p$. An immediate consequence is that not only the red bonds are relevant but also the number of bonds L_B in the blobs diverge. For more details, see (Coniglio (1981, 1982)). Numerical evidence later confirmed the validity of this picture (Pike and Stanley 1981; Hermann and Stanley 1984). In conclusion we can write the following relations

$$y_H = D_p \quad y_T = D_R \quad (28)$$

where $y_H = d - \beta_p/v_p$ is the so-called magnetic field scaling exponent and $y_T = 1/v_p$ is the thermal scaling exponent in the renormalization group language. These results, interestingly, link the critical exponents to the fractal geometry at criticality and may give a hint for the universal character of the critical exponents. Moreover, the fractal structure helps also to understand and predict other phenomena, which occur on a percolating cluster. Indeed one of the motivations for investigating the fractal structure in percolation (Coniglio 1981) was due to some puzzling results, obtained in an interesting series of experimental papers on dilute ferromagnets (Birgeneau et al. 1976, 1980, 1983; Cowley et al. 1977a, b, 1980b, a) using neutron scattering techniques. In their experiments they used different systems which can be modeled by diluted Ising and Heisenberg systems in two and three dimensions and measured, in particular, the critical behavior of the correlation length.

To fix the ideas consider a diluted ferromagnet, in which a fraction $(1 - p)$ of spins randomly chosen are removed. As p decreases the critical temperature $T_c(p)$ decreases, ending into a higher order critical point $Q(T = 0, p = p_c)$. Approaching the Q point along the direction $(T = 0, p \rightarrow p_c)$, the correlation length was found to diverge with an exponent v_p consistent with the percolation exponent for both Ising and Heisenberg systems, as expected (Essam 1980); while along the

direction ($p = 0$, $T \rightarrow 0$), the correlation length was found to diverge with an exponent ν_T , and a crossover exponent $\phi = \nu_p/\nu_T$. For Ising systems the data suggested $\nu_T = \nu_p$ with a crossover exponent $\phi = 1$. However, for Heisenberg systems the thermal exponent ν_T was found different from ν_p with a crossover exponent $\phi \sim 1.5$ in $d = 2$ and $\phi \sim 1.04$ in $d = 3$.

These results have a geometrical explanation in terms of the structure of the infinite cluster. Indeed, using exact renormalization group arguments (Coniglio 1981, 1982), it was found that for Ising systems the thermal scaling exponent $1/\nu_T$ coincide, in any dimension d , with the fractal dimension of the red bonds $D_R = 1/\nu_p$ implying $\nu_T = \nu_p$ with the crossover exponent $\phi = 1$, in agreement with the experimental results and the ϵ expansion (Wallace and Young 1978). For Heisenberg systems instead $1/\nu_T$ coincide with an effective fractal dimension D_ρ of the backbone resistivity L_ρ , defined as $L_\rho \sim \xi^{D_\rho}$, where ξ is the connectedness percolation length (5) and L_ρ is the average resistivity between two points separated by a distance of the order of ξ . Since the backbone resistivity diverges as $L_\rho \sim (p_c - p)^{Z_\rho}$ where Z_ρ is the resistivity exponent, it follows that for diluted Heisenberg systems $D_\rho = Z_\rho/\nu_p$ and $\nu_T = \nu_p/Z_\rho$ with $\phi = Z_\rho$. The resistivity exponent numerically is found to be (Stauffer and Aharony 1994) $Z_\rho \sim 1.4$ in $d = 2$ and $Z_\rho \sim 1.12$ consistent with the experiments, thus explaining the origin of the different crossover exponents for diluted Ising and diluted Heisenberg systems in $2d$ and $3d$. For a general scaling theory and real space renormalization group analysis applied to diluted Ising and Heisenberg systems see also (Stinchcombe 1979a, b, c, 1980).

The above theory (Coniglio 1981, 1982, 1983) not only explains quantitatively the experimental results, but also gives a physical picture of how thermal correlations propagates on the IIC, and why discrete model with discrete symmetry (Ising and Potts models) behave differently from models with continuous symmetry (Heisenberg and n -vector model). Close to $T = 0$ Ising correlation propagates only through the red bonds. As correlation spreads, the spins in the blobs flip coherently altogether acting as one single spin to avoid the

cost of a huge amount of energy. The entire backbone behaves as if it was a one-dimensional chain of length L_R , made only of red bonds. On the other end, for Heisenberg systems the thermal correlations can propagate through the blobs, as the spins with continuous symmetry can tune the rotation of the spins, avoiding to pay a huge amount of energy. With the respect to propagation of Heisenberg correlations, the backbone behaves as if it was a one dimensional chain of length of the order of the resistivity, L_ρ . Note that a model without blobs would give the same lengths $L_R \sim L_\rho$ and therefore the same crossover exponents. This indeed is the case in mean field, namely, for $d \geq 6$, where the blobs are not relevant and the picture of nodes and links (Skal and Shklovskii 1975; de Gennes 1976) holds.

Multifractal Structure of the Incipient Infinite Cluster

In the previous section it has been shown that IIC can be characterized by the fractal dimension of the entire cluster D_p , and the fractal dimension D_R of the red bonds, which are related to the two scaling exponents Eq. (28). Like in standard second order critical phenomena all the other critical exponents can be expressed in terms only of these two scaling exponents. However, percolation transition is much richer than ordinary phase transition. As we have discussed before, other processes can be defined on the percolating cluster, and one needs other critical exponents to describe these processes. One may wonder whether there may be other subset of bonds, whose fractal dimension may be related to such critical exponents. It was indeed shown that the IIC could be further decomposed in infinitely many fractal subsets. This multi-fractal structure was originally proposed for percolation in (de Arcangelis et al. 1985, 1986, 1987) and independently in (Rammal et al. 1985a, b). Their results can be described within the multi fractal formalism of Frish and Parisi (1983; Benzi et al. 1984) and Halsey and collaborators (Halsey et al. 1986). Consider a random resistor network in a box of linear dimension L and associate a unit resistance to each bond of the spanning cluster at p_c . By applying a unit voltage at the opposite boundary of the system,

one can characterize each bond by the voltage V across it. Using numerical simulations and a suitable deterministic model, it was shown (de Arcangelis et al. 1985, 1986, 1987) that the k -moments of the voltage distribution $n(V)$, where $n(V)$ is the number of bonds corresponding to the voltage drop V , scaled with an infinite set of independent exponents dependent on k . This was quite surprising as usually in critical phenomena the moments of the order parameter scale with so-called gap exponent, namely, with an exponent linear in k . From the scaling exponents of the k -moments of the voltage distribution it is possible to derive the scaling behavior of $n(V)$

$$n(V) \sim L^{f(\alpha)} \alpha = -\frac{\ln V}{\ln L} \quad (29)$$

where $f(\alpha)$ is a function of the voltage V . This equation shows that entire IIC can be decomposed in an infinite set of bonds characterized by a value $\alpha(V)$ with fractal dimension $f(\alpha)$. In particular, the set of bonds corresponding to $V = V_{\max}$, where $V_{\max}$ is the maximum value the voltage drop across the bonds, is the set of the red bonds, where the voltage is maximum. Therefore $f(\alpha(V_{\max})) = D_R = 1/\nu_p$. It is also possible to show that the resistivity exponent is linked to the fractal dimension of another subset corresponding to the second moment of the voltage distribution. This fractal dimension is D_ρ , which has been linked, in the previous Sec., to the correlation length exponent ν_T of the diluted Heisenberg model. For more details see (de Arcangelis et al. 1985, 1986, 1987).

Surfaces and Interfaces

The study of the structure of large cluster surfaces and interfaces below p_c has not received as much attention as the study of the IIC internal structure. This problem is relevant to the study of the random composite material dielectric constant, the gel viscosity, the random superconducting network conductivity, and the relative termite diffusion model (de Gennes 1980).

For simplicity, let us consider a random superconducting network, in which superconducting bonds are present with probability p and normal bonds carrying a unit resistance with probability

$1 - p$. For small values of p , we have finite superconducting clusters in a background of normal resistor. As $p \rightarrow p_c$, the superconductivity Σ diverges. For a finite cell of linear dimension L just below p_c , the typical configurations are characterized by two very large clusters almost touching, each one attached to one of two opposite faces. Inside these clusters there are islands of normal resistors. If a unit voltage is applied between the opposite face of the hypercube, there is no current flowing through the bonds in the island. We call these “dead” bonds, in analogy with the dead ends of the percolating cluster. The remaining normal bonds connect one superconducting cluster to the other. These bonds are made of “bridges,” also called “antired bonds,” which have the property that if one is replaced by a superconducting bond, a percolating superconducting cluster is formed. Similarly, to the red bonds, it can be proved (Coniglio 1985) that the fractal dimensionality of the antired bonds is $1/\nu_p$. The proof is based on the following relation which can be proved for any lattice in any dimension

$$(1 - p) \frac{dp_{ij}}{dp} = \mu_{ij}, \quad (30)$$

where p_{ij} is the pair connectedness function (the probability that sites i and j belong to the same cluster) and μ_{ij} is the average number of antired bonds between i and j . These are defined as non-active bonds, such that if one is made active, i and j become connected.

The above considerations suggested that just below p_c the system can be imagined as a superlattice made of large critical clusters whose centers are separated by a distance of the order ξ . The surfaces of these clusters almost touch, and are connected by bridges (antired bonds) and other paths made of more than one bond (Coniglio and Stanley 1984).

Finally, we mention the following result, which relates the size s^* of the critical cluster to the size of its entire perimeter t^* (Stauffer and Aharony 1994; Bunde and Havlin 1991; Havlin and Bunde 1991)

$$t^* = \frac{1-p}{p} s^* - A s^{*\sigma_p}, \quad (31)$$

where $\sigma_p = \frac{1}{v_p D_p}$ is the critical exponent which appears in the cluster number Eq. (11) and A is a constant. The last term $s^{*\sigma_p}$ which appears also in Fisher's droplet model (Fisher 1967a, b, 1971; Fisher and Widom 1969) is usually interpreted as the surface of the droplet. However, if it was a surface, σ_p should satisfy the following bound $\frac{d-1}{d} \leq \sigma_p \leq 1$. The upper bound corresponds to the fully rarefied droplets and the lower bound to compact droplets. Surprisingly enough for the percolation problem σ_p is strictly smaller than $\frac{d-1}{d}$. This paradox can be solved by using a result (Coniglio 1983), which shows that $A s^{*\sigma_p}$ is equal to number of antired bonds between critical cluster separated by a distance of order ξ . Since the subset of antired bonds is only a subset of the entire perimeter, it explains why $\sigma_p < \frac{d-1}{d}$. This result gives the best geometrical interpretation of the thermal scaling exponent y_T . It indeed shows that $y_T = D_{AR}$, where D_{AR} is the fractal dimension of the antired bonds, namely, that part of the surface which contributes to the surface tension.

Percolation in the Ising Model

In this section we want to extend the percolation problem to the case in which the particles are correlated. The simplest model to consider is the lattice gas or Ising model. In the following, we will use the Ising terminology. We know that Ising model exhibits a thermodynamic transition for zero external field, $H = 0$, at a critical temperature T_c . The question that we ask is how the percolation properties are modified due to the presence of correlation. We first consider the case when the cluster are made of nearest neighbor down spins (section “Ising Clusters”). Later, in section “Ising Droplets,” we will modify the cluster definition in such a way that these new clusters describe the thermal fluctuations, namely, we require that the clusters satisfy the same properties as the droplets in Fisher's droplet model (Fisher (1967a), Fisher (1967b), Fisher (1971), Fisher and Widom

(1969)). Namely: (i) the size of the clusters must diverge at the Ising critical points, (ii) the linear dimension of the clusters must diverge with the same exponent as the correlation length, and (iii) the mean cluster size must diverge with the same exponent as the susceptibility.

These conditions are satisfied if the cluster size distribution for zero external field has the following form

$$n(s, T) = s^{-\tau} f((T - T_c) s^\sigma). \quad (32)$$

The parameters σ and τ are related to critical exponents α , β , and γ through Eqs. (12) and (13), where now α , β and γ are the Ising critical exponents. In particular for $d = 2$, $\sigma = 8/15 \simeq 0.53$ and $\tau = 31/15 \simeq 2.07$, and for $d = 3$, $\sigma \simeq 0.64$ and $\tau \simeq 2.21$.

Ising Clusters

The Hamiltonian of the Ising model is given by:

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i \quad (33)$$

where $S_i = \pm 1$ are the spin variables, J is the interaction between two nearest neighbor (nn) spins, and H is the magnetic field. From the thermodynamic point of view, the only quantities of interest are those, which can be obtained from the free energy, and those were the only quantities that Onsager was concerned with in his famous solution of the $2d$ Ising model. However one can look at the Ising model from a different perspective by studying the connectivity properties using concepts such as clusters (Binder 1976; Binder and Müller-Krumbhaar 1974; Odagaki et al. 1975), which have been systematically elaborated in percolation theory. There are two reasons for approaching the problem also from the connectivity point of view. One reason is that it gives a better understanding of the mechanism of the phase transition (Fisher (1967a), Fisher (1967b), Fisher (1971), Fisher and Widom (1969)). Indeed, concepts like universality and scaling have been better understood in terms of geometrical clusters and

fractal dimensions (Coniglio 1989). A second reason is that there are physical quantities amenable to experimental observations, which are associated to the connectivity properties and cannot be obtained from the free energy. It is very important to note however that the definition of connectivity, and therefore the definition of the cluster, is not always the same, but may depend on the particular observable associated to it.

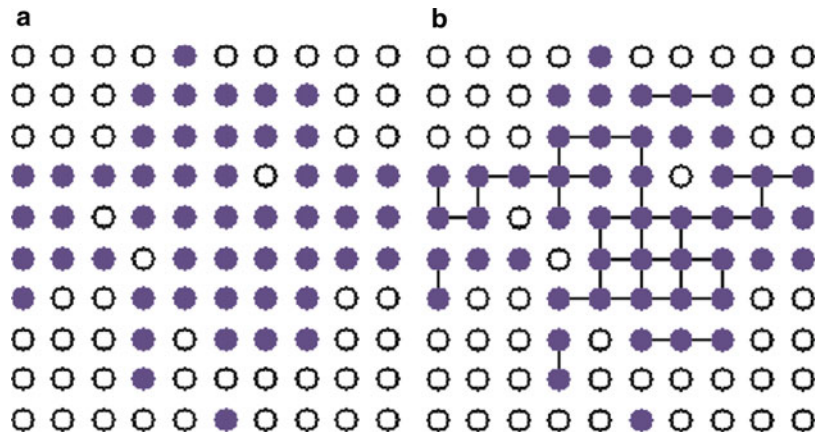
In the Ising model, for a given configuration of spins it is rather natural to define a cluster as a maximal set of nn down parallel spins (Fig. 1) (The Ising Hamiltonian, Eq. (33), is equivalent to the lattice gas Hamiltonian $\mathcal{H}_{LG} = -J'\sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i$, with $n_i = (1 - S_i)/2$, $J' = 4J$ and $\mu = 2H - 4J$. In the lattice gas terminology an Ising cluster is a maximal set of nn occupied sites.). For some time, these clusters were believed to be responsible for the correlations present in the Ising model. This idea was also based on numerical results which showed evidence that in two dimensions the mean cluster size diverges at the thermal critical point (Binder 1976). However, the idea that the clusters could describe thermal correlations was abandoned when it was shown, by numerical simulations, in the three dimensional Ising model (Müller-Krumbhaar 1974) and by exact solution on the Bethe lattice (Coniglio 1976), that the percolation point appeared in the low density phase of down spins on the coexistence curve at a temperature T_p before the critical point T_c is reached ($T_p < T_c$).

At the same time, it was suggested by topological arguments (Coniglio 1975) that only in two dimensions the critical point coincides with the percolation point, but not necessarily in higher dimensions. The arguments followed two steps: in the first step it was argued that an infinite cluster of up spins is a necessary condition for having a spontaneous magnetization. This implies a percolation transition of down spins on the coexistence curve $T_p \leq T_c$, in the second step it was argued that due to topological reasons in two dimensions, it is not possible to have an infinite cluster of up spins, with density larger than zero, coexisting with an infinite cluster of down spins, which implies $T_p \geq T_c$. Combining with the previous inequalities one obtains in two dimensions $T_p = T_c$. Later these results were proven rigorously (Coniglio et al. 1976, 1977c) along with many other results relating connectivity and thermodynamic quantities. For more details, we refer to the original papers.

It is clear that the Ising clusters, defined as group of nn parallel spins, do not have the property of describing correlated regions corresponding to spin fluctuations, as originally expected. Indeed, even in two dimensions, where the thermal critical point coincides with the percolation point, the Ising clusters were not suitable for such description. Series expansion showed that the mean cluster size diverges with an exponent, $\gamma^* = 1.91 \pm 0.001$, rather different from the susceptibility exponent, $\gamma = 1.75$ (Sykes and Gaunt 1976). Later it has been shown exactly that $\gamma^* = 91/48$ (Stella and Vanderzande 1989).

Correlated Percolation,

Fig. 1 (a) Ising configuration at T_c : “down” spins are represented by filled circles. (b) Correct clusters are obtained from the configuration given in (a) by putting bonds between occupied sites with probability $p = 1 - e^{-2\beta J}$



Ising Droplets

From the properties mentioned in section “[Ising Clusters](#),” it appears that the Ising clusters are too big to describe the proper droplets. The reason is that there are two contributions to the Ising clusters. One is due to correlations, the second has a pure geometrical origin. In fact, two nn spins even in absence of correlations have a finite probability of being parallel. This geometrical contribution becomes evident in the limit of infinite temperature and zero external field. In this case, although there is no correlations and the susceptibility is zero, the cluster size is different from zero. Indeed, in $3d$ at infinite temperature there is even an infinite cluster of “up” and “down” spins.

Binder (1976) proposed to cut the infinite cluster in order to have $T_p = T_c$ in $d = 3$, but he did not give the microscopic prescription to do it. Later, Coniglio and Klein (1980) proposed to reduce the cluster size by introducing fictitious bonds between nn parallel spins with probability p_b (Fig. 1). These new clusters are made of nn parallel spins connected by bonds. The original Ising cluster will either reduce its size or will break into smaller clusters. A Hamiltonian formalism was proposed to study site correlated percolation (Murata 1979) corresponding to $p_b = 1$. This formalism was generalized in (Coniglio and Klein 1980) to study site-bond correlated percolation $p_b \neq 1$. The resulting hamiltonian formalism is given by the Potts lattice gas model, a model introduced in (Berker et al. 1978; Nienhuis et al. 1979) in a different context. Here we consider a slightly modified version, corresponding to the following dilute Ising s -state Potts Model (DIPM):

$$-\mathcal{H}_{DP} = J_b \sum_{\langle ij \rangle} (\delta_{\sigma_i \sigma_j} - 1) (S_i S_j + 1) + J \sum_{\langle ij \rangle} S_i S_j, \quad (34)$$

where $\sigma_i = 1, \dots, s$ are Potts variables and the sum is over all nearest neighbor sites. In the same way as the s -state Potts model in the limit $s = 1$ (Wu 1982) describes the random bond percolation model, the DIPM describes percolation in the

Ising model with zero external field, where the clusters are made of parallel spins connected by bonds with probability, $p_b = 1 - e^{-2\beta J_b}$.

In particular, the average number of clusters G , that plays the role of the free energy in the percolation problem, is given by $G = dF/ds|_{s=1}$, where

$$-\beta F = \lim_{N \rightarrow \infty} \frac{1}{N} \ln \left(\sum_{\{\sigma_i S_i\}} e^{-\beta \mathcal{H}_{DP}} \right). \quad (35)$$

The model exhibits the interesting properties that, by choosing $J_b = J$, it coincides with a pure $2s$ -state Potts model. Therefore, in the limit $s = 1$ the DIPM coincides with the $s = 2$ Potts model, namely, with the Ising model. Consequently, F becomes the Ising model free energy and G has a singularity at the Ising critical point. This argument immediately suggested that the site-bond correlated percolation for $J_b = J$, namely, with the bond probability given by

$$p_b \equiv p = 1 - e^{-2\beta J}, \quad (36)$$

should reproduce the same critical behavior of the Ising model. Namely, the percolation quantities become critical at the Ising critical point in the same way as the corresponding thermal quantities.

Indeed using real space renormalization group arguments (Coniglio and Klein 1980), it was possible to show that the size of the clusters of parallel spins, connected by bonds with probability p_b , given by Eq. (36), diverges at the Ising critical point with Ising exponents, exhibiting thus the same properties as the droplets in Fisher’s model. These clusters were called droplets to distinguish them from the Ising clusters. This concept of droplets to describe the phase transition in terms of geometrical cluster has been fruitful in understanding other complex phenomena (Binder 2017). Such droplets for example have been used to properly describe nucleation theory (Stauffer et al. 1982b; Binder and Virnau 2016; Schmitz et al. 2013) and has been applied to a variety fields such as nuclear physics (Ma 1999; Ma et al. 2004), Gauge Theory (Fortunato and Satz 2000a, b), $O(n)$ models

(Bialas et al. 2000; Blanchard et al. 2000), fragmentation (Campi and Krivine 2005; Campi et al. 2003; Mader et al. 2003), microemulsions (Cazabat 1983), phase behavior of particles with limited valence (Tartaglia and Sciortino 2010), and others.

Droplets in an External Field

By keeping the same definition of droplets given above, in the case of an Ising model in an external field $H > 0$ one finds a phase diagram in the H, T plane or in the M, T plane, with a percolation line of “down” spins ending at the Ising critical point (see Fig. 2). Along the percolation line one finds critical exponents in the universality class of random percolation, with a cross-over to Ising critical exponents as the Ising critical point is approached (Coniglio and Klein 1980). In this context the Ising critical point is a higher order critical point for the percolation transition. This percolation line, also known as the Kertesz line, has received some attention (Stauffer and Aharony 1994; Kertesz 1989; Stauffer 1990; Wang 1989) (see for more details the review by Sator (2003)). Although the Ising free energy has no singularity along this line some physical interpretation has been suggested for the Kertesz line (Campi et al. 2001).

On the other hand, this line disappears if the droplet definition is modified in the presence of an external field (Coniglio et al. 1989; Wang 1989), according to Fortuin and Kasteleyn formalism

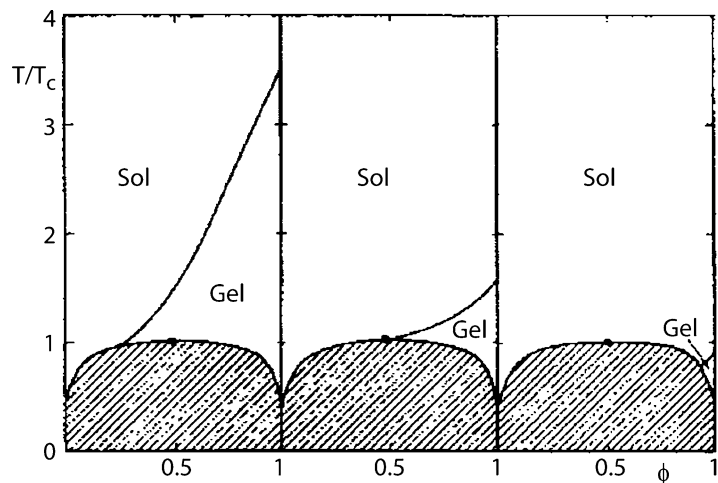
(Kasteleyn and Fortuin 1969; Fortuin and Kasteleyn 1972) and Swendsen and Wang approach (Swendsen and Wang 1987). In this approach the field is treated as a new interaction between each spin and a ghost site. Consequently, for positive H (negative H) an “up” (“down”) spin can be connected to the ghost spin with a probability $p_H = 1 - e^{-2\beta |H|}$. Droplets now are defined as a maximal set of spins connected by bonds, where, as before the bonds between nearest neighbor parallel spins have probability P_b given by Eq. (36) and p_H between spins and the ghost spin. Note that two far away spins can be easily connected through the ghost spin. In this way the presence of a positive (negative) magnetic field implies always the presence of an infinite cluster of “up” (“down”) spins.

Exact Relations Between Connectivity and Thermal Properties

Interestingly, it was also shown (Coniglio et al. 1989) that the droplets so defined with and without the external field have the same statistics of the clusters in the random cluster model introduced by Fortuin and Kasteleyn (FK) (Kasteleyn and Fortuin (1969), Fortuin and Kasteleyn (1972)) (see section “Fortuin Kasteleyn-Random Cluster Model”), although the CK droplets and the FK clusters have a different meaning. Using the relations between the connectivity properties of the random cluster model and the thermal properties of the Ising model, it was finally possible to prove

Correlated Percolation,

Fig. 2 Montecarlo simulations of the 3d lattice gas model for three values of the bond probability $p_b = 1 - e^{-2c\beta J}$ with the constant $c = 2.25, 1, 0.564$ from left to right. Φ is the density of down spins. The Gel and the Sol indicates the percolation and non percolation phase. (From Kertesz et al. 1983)



formally that in any dimension and for any temperature T and external field $H \geq 0$, the following relations between connectivity and thermal properties hold Coniglio et al. (1989):

$$\begin{cases} \rho_\infty = m \\ p_{ij} = g_{ij} \end{cases} \quad (37)$$

where ρ_∞ is the density of up spins in the percolating droplet, m is the magnetization per site, p_{ij} is the probability that i and j are connected (through both finite or infinite droplet) and $g_{ij} = \langle S_i S_j \rangle$.

In particular, for $T > T_c$ and zero external field $H \rightarrow 0$, we have that the magnetization $m = 0$ and g_{ij} coincides with the spin-spin pair correlation function. Consequently $\rho_\infty = 0$, namely, the probability for a spin to be in an infinite droplet is zero, and therefore p_{ij} coincides with the probability that two spins i and j are in the same finite droplet. For $T < T_c$ instead we have $\rho_\infty = m > 0$, and $p_{ij} = p_{ij}^f + p_{ij}^\infty$, where $p_{ij}^f(p_{ij}^\infty)$ is the probability that spins in i and j are in a finite (infinite) droplet. From Eq. (37) it follows for $T < T_c$:

$$p_{ij}^f + p_{ij}^\infty - \rho_\infty^3 = \langle S_i S_j \rangle - m^2. \quad (38)$$

By summing over i and j we have

$$S + (\Delta\rho_\infty)^2 = \chi, \quad (39)$$

where S is the mean cluster size of the finite clusters, $(\Delta\rho_\infty)^2$ is the fluctuation of the density of the infinite cluster and χ is the susceptibility. These exact results show that above T_c mean cluster size and susceptibility coincide, while below T_c there are two contributions to the susceptibility, one due to the mean cluster size and the second related to the fluctuation of the density of the infinity cluster. Monte Carlo calculations (Rousseny et al. 1982) show that both terms have the same critical behavior as also occurs in random percolation (Coniglio and Stauffer 1980; Chayes et al. 1989), so the mean cluster size S diverges like the susceptibility. We expect that this is the case for dimensions up to $d = 4$, the upper critical dimensionality of the Ising model.

In mean field, as we will see, the mean cluster size below T_c diverges with an exponent different from the susceptibility.

One very interesting application based on the CK-FK approach was produced by Swendsen and Wang (1987, 1990), who elaborated a cluster dynamics which drastically reduced the slowing down near the critical point of the Ising and Potts model (see also Wolff (1988), (1989a), (1989b) for further developments).

The droplet definition can be extended to the nn antiferromagnetic Ising model (Amitrano et al. 1983) and to the Ising model with any ferromagnetic interaction J_{ij} between sites i and j (Jan et al. 1982). In this case, the CK clusters are defined as set of parallel spins connected by bonds present between i and j with probability $p_{ij} = 1 - e^{-2\beta J_{ij}}$. It can be shown that also in this case, the relations, Eq. (37), between connectivity and thermal quantities hold.

Droplets in Two and Three Dimensions

The percolation properties of the droplets problem has been studied, by real space renormalization group in two dimensions (Coniglio and Klein 1980; Coniglio and Zia 1982), by ϵ expansion, near six dimensions (Coniglio and Lubensky 1980) and by Monte Carlo in two and three dimensions (Stauffer 1981; Heermann and Stauffer 1981; Rousseny et al. 1982; Jan et al. 1982; D'Onorio De Meo et al. 1990).

The renormalization group analysis shows that in $2d$, the Ising critical point is a percolation point for down or up spins connected by bonds for all values of bond probability, such that $1 \leq p_b < 1 - e^{-2\beta J}$. The fractal dimension $D^* = (\gamma^*/\nu + 2)/2 = 187/96$ (Stella and Vanderzande 1989), being higher than the fractal dimension $D = (\gamma/\nu + 2)/2 = 15/8$ for the value of $p_b \equiv p = 1 - e^{-2\beta J}$.

In the renormalization group language this means that there are two fixed points, one corresponding to the universality class of the Ising cluster, the other one corresponding to the droplets. In the first one, the variable J_b is irrelevant, namely, the scaling exponent associated to it, $y_b < 0$. In the second fixed point associated to the droplets instead $y_b > 0$. The result that the Ising critical point is a percolation point for a

range of values of p_b , at the first sight seems counter-intuitive. Indeed, if the Ising critical point corresponds to the onset of percolation for Ising clusters ($p_b = 1$), one would expect that for $p_b < 1$ the clusters would not percolate anymore. The puzzle can be clarified by studying the fractal structure of the Ising clusters and the droplets at T_c (Coniglio 1989). Indeed, it can be shown that y_b is the scaling exponent of the red bonds, namely, $L_R \sim l^{y_b}$ where L_R is the number of red bonds between two connected sites separated by a distance of the order l , consequently the droplets, characterized by $y_b > 0$, are made of links and blobs, like in random percolation. Due to the presence of links, the cluster breaks apart and does not percolate anymore as the bond probability decreases. On the contrary the Ising clusters ($p_b = 1$), characterized by $y_b < 0$, are made only of blobs and no links, therefore by decreasing the bond probability the infinite cluster does not break and still percolates, until $p_b = p$.

In $3d$ at the Ising critical point, T_c , there is an analogous line of anomalous percolation point for clusters of down spins connected by bonds, for all values of bond probability such that $1 \leq p_b < 1 - e^{-2\beta J}$, although the probability P_∞ , for a down spin to be in the infinite cluster is different from zero. More precisely the quantity $p_{ij} - P_\infty^2$ decays as a power law, where p_{ij} is the probability that i and j are connected. For more details see (Coniglio and Figari 1983). As p_b decreases towards $p = 1 - e^{-2\beta J}$ there is a cross-over towards a different power law characterized by the Ising exponent, while P_∞ , goes to 0.

Ising Droplets above $d = 4$

In section “[Exact Relations Between Connectivity and Thermal Properties](#)” we have reported the relations Eqs. (37) and (38), which are exact and are valid in any dimension including mean field. As a matter of fact in mean field, the percolation order parameter and the magnetization are identical and go to zero with the exponent $\beta = 1/2$, while the mean cluster size above T_c coincides with the susceptibility and diverges with the exponent $\gamma = 1$. The same is true for the connectedness length above T_c , which coincides with the

correlation length, and diverges with an exponent $\nu = 1/2$. However below T_c the mean cluster size diverges with an exponent $\gamma' = 1/2$ and the correlation length with an exponent $\nu' = 1/4$ (Coniglio et al. 1979, 1982, 1989; Chayes et al. 1999). This result is a consequence that the two terms in Eq. (38), the probability that two sites are in the same finite droplet, p_{ij}^f , and the correlation of the infinite droplet density at site i and j , $p_{ij}^\infty - \rho_\infty^2$, do not scale in the same way, giving rise to two lengths, diverging respectively with exponents ν' and ν .

These somehow anomalous results are probably a consequence that the Ising model has an upper critical dimension $d_c = 4$ while the DIPM which describes the droplet problem has an upper critical dimension $d_c = 6$ (Coniglio and Lubensky 1980). Indeed there are arguments that for $4 \leq d \leq 6$ below T_c the critical exponents are $\nu' = \frac{1}{d-2}$, $\gamma' = \frac{2}{d-2}$, $\beta = 1/2$, $\eta = 0$ and fractal dimension $D_p = \frac{1}{2}(d+2)$, with an upper critical dimension $d_c = 6$. Of course for $T > T_c$ the exponents are $\gamma = 1$, $\nu = 1/2$ and $\eta = 0$.

Due to the breakdown of the mapping between thermal fluctuations and mean cluster size below T_c above $d = 4$, it is not possible to extend easily the geometrical picture, employed in random percolation, to explain the breakdown of hyperscaling in the Ising model. For a study of droplets inside the metastable region see Klein et al. (2000), Padoa Schioppa and Sciortino (1998), Heermann et al. (1984).

Generalization to the q -state Potts Model

All the results found for the Ising case have been extended (Coniglio and Peruggi 1982) to the q -state Potts model. This model is defined by the following Hamiltonian:

$$-\mathcal{H}_q = qJ \sum_{\langle ij \rangle} \delta_{\sigma_i \sigma_j}, \quad (40)$$

where the spin variables σ_i can assume q values, $\sigma_i = 1, \dots, q$. This model coincides with the Ising model for $q = 2$, reproduces the random percolation problem in the limit $q = 1$ and the tree percolation model in the limit $q = 0$ (Wu 1982).

The geometrical approach developed in the previous sections for the Ising model can be extended to the q -state Potts model. In particular one can define the site-bond Potts correlated percolation, where clusters are made of nn spins in the same state, connected by bonds with bond probability p_b . By choosing $p_b = p = 1 - e^{-q\beta J}$, it is possible to show that these clusters percolate at the Potts critical temperature $T_c(q)$, with percolation exponents identical to the thermal exponents, and therefore, behave as the critical droplets.

The formalism is based on the following diluted Potts model (Coniglio and Peruggi 1982; Temesvari 1984; Janke and Schakel 2004; Qian et al. 2005; Deng et al. 2005; Balog and Uzelac 2007):

$$-\mathcal{H}_{DP}^q = J_b \sum_{\langle ij \rangle} (\delta_{\tau_i \tau_j} - 1) \delta_{\sigma_i \sigma_j} + qJ \sum_{\langle ij \rangle} \delta_{\sigma_i \sigma_j}, \quad (41)$$

where the second term, which controls the distribution of spin variables, is the q -state Potts Hamiltonian, whereas the first term contains auxiliary Potts variables $\tau_i = 1, 2, \dots, s$ and controls the bonds distribution.

As in the Ising case, the Hamiltonian, Eq. (41), in the limit $s \rightarrow 1$ describes the site-bond Potts correlated percolation problem with p_b given by $p_b = 1 - e^{-\beta J_b}$. The droplets are obtained in the particular case $J_b = qJ$. For this value indeed Hamiltonian, Eq. (41), for $s \rightarrow 1$ coincides with the q -state Potts model. As for the Ising case, it is also possible to show (Coniglio et al. 1989) that the statistics of the q -state Potts droplets coincides with the statistics of the random cluster model for any value of q .

Once the Ising and Potts model has been mapped onto a percolation problem, we can extend some of the results of random percolation to thermal problems.

Fractal Structure in the Potts Model: Links and Blobs

Like in random percolation, also in the q -state Potts model it can be shown that at $T_c(q)$

the critical droplets have a fractal structure made of links and blobs, with a fractal dimension $D(q) = d - \beta(q)/\nu(q)$, where $\beta(q)$ and $\nu(q)$ are, respectively, the order parameter and correlation length exponent. Therefore, $D(q)$ coincides with the magnetic scaling exponent $y_H(q)$ (Nienhuis et al. 1980). However, the fractal dimension of the red bonds $D_R(q)$ does not coincide with the thermal scaling exponent $y_T(q)$ (den Nijs 1979), associated to the thermal variable J , like in random percolation. Instead $D_R(q)$ is found to coincide with the bond probability scaling exponent $y_b(q)$ associated to the variable J_b in the Hamiltonian, Eq. (41) (Coniglio 1989). Only for $q = 1$ the thermal scaling exponent and the probability scaling exponents coincide, consequently $y_T(1) = y_b(1) = D_R(1)$. Using the mapping from the Potts model to the Coulomb gas (Saleur and Duplantier 1987; Duplantier and Saleur 1989), it is possible to obtain the exact value of the fractal dimension of the red bonds $D_R(q)$ and of the external perimeter or hull $D_H(q)$ in the FK random cluster model. Given that the geometrical properties of the random cluster model coincide with those of the Potts droplets, $D_R(q)$ and $D_H(q)$ provide also the fractal dimension of the red bonds and of the hull of the Potts droplets (Coniglio 1989). Finally, note that since $D_R(q) = y_b(q)$, the values of $D_R(q)$ provides also the exact values of the scaling exponent $y_b(q)$ associated to the variable J_b in the Hamiltonian, Eq. (41). As matter of fact, using conformal invariance theory, applied to the Hamiltonian Eq. (41) for $q = 2$, it was found $y_b(2) = 13/24$ (Stella and Vanderzande 1989) in agreement with the value $D_R(2) = 13/24$ (see table). For more results see also Blote et al. (1992).

From Table 1, it appears that the exact value of $D(q)$ does not vary substantially with q , for $d = 2$. This observation can be understood by noting that, using this geometrical approach, the driving mechanism of the critical behavior can be viewed as coalescence of clusters just like in random percolation. Then one would expect for any q that the fractal dimension should be close to the fractal dimension of the critical clusters in the percolation problem. This also explains the observation of Suzuki (1974), known as strong universality, that for a large class of models the

Correlated Percolation, Table 1 Fractal dimensions, for $d = 2$, of the whole cluster (D), of the Hull (D_H), and of the red bonds (D_R) for the Potts droplets. It is also reported the thermal power exponent γ_T

q	D	γ_T	D_H	D_R
0	2	0	2	5/4
1	91/48	3/4	7/4	3/4
2	15/8	1	5/3	13/24
3	28/15	6/5	8/5	7/20
4	15/8	3/2	3/2	0

ratio γ/ν or β/ν do not vary appreciably. Since these ratios of critical exponents for fixed d depend only on the magnetic scaling exponent, which is identical to the fractal dimension, the strong universality is consequence of the quasi-universal feature of the fractal dimension as discussed above. Unlikely the fractal dimension of the whole cluster, $D_R(q)$ and $D_H(q)$ do change substantially and characterize the different models as function of q . Particularly sensitive to q is the fractal dimension of the red bonds, which has its largest value at $q = 0$ (tree percolation), where the backbone is made only of links. As q approaches q_c the cluster becomes less ramified until the red bonds vanish ($D_R(4) = 0$). This results in a drastic structural change from a links and blobs picture to a blobs picture only, anticipating a first order transition. Interestingly, the fractal dimension of the red bonds for $q = 0$, $D_R = 5/4$ has been related to the abelian sandpile model (Dhar 1999). The reason why $D_R(q)$ is so model dependent is due to the fact that the fractal set of the red bonds is only a small subset of the entire droplet, and therefore, this “detail” is strongly model dependent. Also, the thermal exponent $\gamma_T(q)$ is strongly model dependent; however, so far it has not been found the geometrical characterization in terms of a fractal dimension for such exponent except $q = 1$ (random percolation).

Fortuin Kasteleyn-Random Cluster Model

We will present here the random cluster model introduced by Fortuin and Kasteleyn. Let us consider the q -state Potts model on a d -dimensional hypercubic lattice. By freezing and

deleting each interaction of the Hamiltonian (see Appendix), they managed to write the partition function of the Potts model, $Z = \sum_{\{\sigma_i\}} e^{-\beta \mathcal{H}_q}$, in the following way

$$Z = \sum_C p^{|C|} (1-p)^{|A|} q^{N_C}, \quad (42)$$

where C is a configuration of bonds defined in the same hypercubic lattice, just like a bond configuration in the standard percolation model, $|C|$ and $|A|$ are, respectively, the number of bonds present and absent in the configuration C , and N_C is the number of clusters in the configuration C .

In conclusion, in the FK formalism the partition function of the Potts model is identical to the partition function, Eq. (42), of a correlated bond percolation model (Kasteleyn and Fortuin 1969; Fortuin and Kasteleyn 1972; Hu 1984, 1992; Hu and Mak 1989) where the weight of each bond configuration C is given by

$$W(C) = p^{|C|} (1-p)^{|A|} q^{N_C} \quad (43)$$

which coincides with the weight of the random percolation except for the extra factor q^{N_C} . They called this particular correlated bond percolation model, the random cluster model. Clearly for $q = 1$ the cluster model coincides with the random percolation model.

Fortuin and Kasteleyn have related the percolation quantities associated to the random cluster model to the corresponding thermal quantities in the q -state Potts model (Kasteleyn and Fortuin 1969; Fortuin and Kasteleyn 1972). In particular for the Ising case, $q = 2$,

$$|\langle S_i \rangle| = \langle \gamma_i^\infty \rangle_W \quad (44)$$

and

$$\langle S_i S_j \rangle = \langle \gamma_{ij} \rangle_W, \quad (45)$$

where $\langle \dots \rangle$ is the Boltzmann average and $\langle \dots \rangle_W$ is the average over bond configurations in the bond correlated percolation with weights given

by Eq. (43). Here $\gamma_i^\infty(C)$ is equal to 1 if the spin at i belongs to the infinite cluster, 0 otherwise; $\gamma_{ij}(C)$ is equal to 1 if the spins at sites i and j belong to the same cluster, 0 otherwise.

Interestingly, the connectivity properties in the FK random cluster model can be related (Coniglio et al. 1989) to the CK droplets:

$$\rho_\infty = \langle \gamma_i^\infty \rangle_W, \quad (46)$$

$$p_{ij} = \langle \gamma_{ij} \rangle_W, \quad (47)$$

where ρ_∞ is the density in the infinite droplet and p_{ij} is the probability that i and j is the pair connectdness function for the droplets as defined in section “Exact Relations Between Connectivity and Thermal Properties.” From Eqs. (44), (45), (46), and (47) it follows Eqs. (37).

Hill's Clusters

In this section we discuss the possibility to extend the definition of droplets to simple fluids. In 1955 Hill (1955) introduced the concept of physical clusters in a fluid in an attempt to explain the phenomenon of condensation from a gas to a liquid. In a fluid made of particles interacting via a pair potential $u(r)$, physical clusters are defined as a group of particles pairwise bounded. A pair of particles is bounded if in the reference frame of their center of mass their total energy is less than zero. Namely, their relative kinetic energy plus the potential energy is less than zero. The probability that two particles at distance r are bounded can be calculated (Hill 1955) and is given by

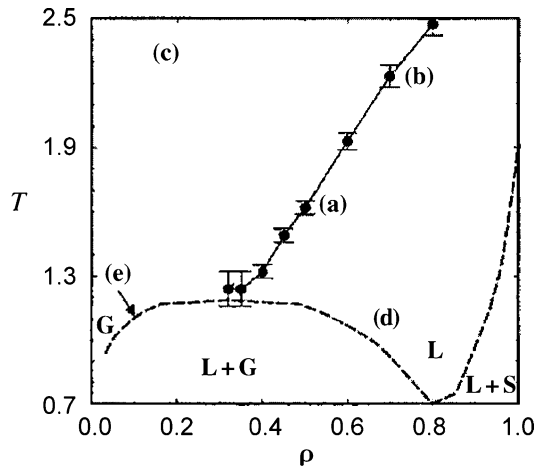
$$p_H(r) = \frac{4}{\pi} \int_0^{\sqrt{-\beta u(r)}} x^2 e^{-x^2} dx. \quad (48)$$

More recently it was noted (Campi et al. 1999) that the bond probability, Eq. (48), calculated for the three dimensional nm lattice gas model, is almost coincident with the bond probability p of Eq. (36). This implies that Hill's physical clusters for the $3d$ lattice gas almost coincide with the

droplets defined by Coniglio and Klein, and indeed Hill's clusters percolate along a line almost indistinguishable from the droplets percolation line (see Fig. 2).

In order to calculate percolation quantities in a fluid, in (Coniglio et al. 1977a, b) the authors developed a theory based on Mayer's expansion. In particular, using this theory they calculated analytically, for a potential made of hard core plus an attractive interaction, the percolation line of Hill's physical clusters in a crude mean field approximation and compared with the liquid gas coexistence curve. They found that the percolation line ended just below the critical point in the low-density phase but not exactly at the critical point. For further developments of the theory see (Given and Stell 1991).

Recently (Campi et al. 2001), using molecular dynamics, the percolation line of Hill's physical clusters was calculated for a Lennard–Jones potential. The results showed a percolation line ending close or at the critical point (Fig. 3) suggesting that Hill's clusters are good candidates to describe the density fluctuations like the droplets in the lattice gas model, although there is no proof of relations analogous to those valid for the droplets in the lattice gas such as Eq. (37), which



Correlated Percolation, Fig. 3 Phase diagram of the Lennard–Jones fluid using molecular dynamics. The full line corresponds to percolation of cluster following Hill's definition. (From Campi et al. 2001)

would prove that their size would diverge exactly at the critical point with thermal exponents.

Although Hill's clusters may represent the critical fluctuations near the critical point, we may wonder whether they have a physical meaning away from the critical point. In particular, we may wonder whether we can detect experimentally the percolation line in the phase diagram. In a Lennard-Jones fluid, molecular dynamics shows that quantities such as viscosity or diffusion coefficient do not seem to exhibit any anomalous behavior through the percolation line (Campi et al. 2001). In some colloids instead the percolation line is detected through a steep increase of the viscosity. What would be the difference in the two cases? The difference may rely in their lifetime. The possibility to detect the percolation line of these clusters is expected to depend on the lifetime of the clusters, which in turn depends on the bond lifetime. The larger is the cluster lifetime the larger is the increase of the viscosity, the better the percolation line can be detected. In section “Scaling Behavior of the Viscosity,” we will discuss the behavior of the viscosity as function of the lifetime of the clusters.

Clusters in Weak and Strong Gels

In the previous section we have shown the case in which the probability of having a bond between two particles coincides with the probability that the two particles form a bound state defined according to Hill's criterion. Now we want to show another mechanism leading to the formation of bound states, which is more appropriate to gels. The importance of connectivity in gels was first emphasized by Flory (1941, 1979). The application of percolation theory to gels was later suggested by de Gennes (1975, 1979) and Stauffer (Stauffer 1976; Stauffer et al. 1982a). Here we consider a system made of monomers in a solvent. Following (Coniglio et al. 1979, 1982) we shall assume that the monomers can interact with each other in two ways. One is the usual van der Waals interaction, and the other is a directional interaction that leads to a chemical bond. A simple model for such a system is a lattice gas model where an

occupied site represents a monomer and an empty site a solvent. For simplicity we can put equal to zero the monomersolvent interaction and the solvent-solvent interaction, and include such interaction in an effective monomer-monomer interaction. The monomer-monomer interaction ε_{ij} can reasonably be approximated by a nearest neighbor interaction

$$\varepsilon_{ij} = \begin{cases} -W \\ -E \end{cases} \quad (49)$$

where $-W$ is the van der Waals type of attraction and $-E$ is the bonding energy. Of course, this second interaction, which is the chemical interaction, occurs only when the monomers are in particular configurations. For simplicity we can suppose that there is 1 configuration which corresponds to the interaction of strength E , and Ω configurations which corresponds to the interaction of strength W . We expect $E \gg W$ and $\Omega \gg 1$. It can be easily calculated (Coniglio et al. 1979, 1982) that such a system is equivalent to a lattice gas model with an effective nn interaction $-\varepsilon$ given by

$$e^{\beta\varepsilon} = e^{\beta E} + \Omega e^{\beta W}. \quad (50)$$

Therefore, from the static point of view the system exhibits a coexistence curve and a critical temperature which characterizes the thermodynamics of the system. However, the system microscopically behaves rather different from a standard lattice gas. Indeed, in a configuration in which two monomers are nn , in a standard lattice gas they feel one interaction, while in the system considered here with some probability p_b they feel a strong chemical interaction $-E$ and with probability $1 - p_b$ they feel a much smaller interaction $-W$. The probability p_b can be easily calculated and is given by

$$p_b = \frac{e^{\beta E}}{e^{\beta E} + \Omega e^{\beta W}}. \quad (51)$$

In conclusion, the system from the static point of view is equivalent to a lattice gas with

interaction ε given by Eq. (50). However, we can also study the percolation line of the clusters made by monomers connected by chemical bonds. This can be done by introducing bonds between nn particles in the lattice gas with nn interactions, the bonds being present with probability p_b given by Eq. (51). By changing the solvent, the effective interaction W changes and one can realizes three cases topologically similar to those of Fig. 2, where the percolation line ends at the critical point or below the critical point in the low-density or high-density phase (for more details see (Coniglio et al. 1979, 1982)).

The lifetime of the bonds is of the order of $e^{\beta E}$. Since E is very large the lifetime could be very large. For an infinite bond lifetime the bonded clusters are permanent and the viscosity diverges due to the divergence of the mean cluster size (see for example Stauffer et al. 1982a), and the percolation line can be easily detected. We consider three particular physical systems, which could be rather emblematic of a general situation where the percolation line has been detected:

- (a) Microemulsions of water in oil (Chen et al. 1994).
- (b) Triblock copolymers in unicellar systems (Mallamace et al. 2000, 1999).
- (c) Gelatin water methanol systems (Tanaka et al. 1979).

In Figs. 4, 5, and 6, we show respectively the phase diagram of the systems (a), (b), (c), where it is shown the coexistence curve in the temperature-concentration diagram, together with “percolation lines.”

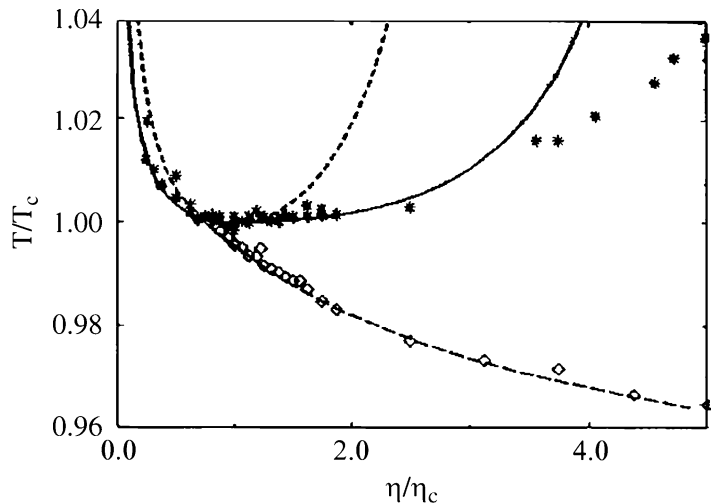
In particular, in (a) the system consists of three components AOT/water/decane. For the temperature and the concentration of interest, the system can be considered as made of small droplets of oil surrounded by water in a solvent. The droplets interact via a hard-core potential plus short-range attractive interaction. Because of the entropic nature of the attractive interaction, the coexistence curve is “upside-down” with the critical point being the minimum instead of the maximum (Fig. 4). The broken line is characterized by a steep increase of conductivity.

In (b), the system is made of triblock copolymers unicellar in water solution, c is the volume fraction of the unicelles (Fig. 5). The line is characterized by a steep increase in the viscosity.

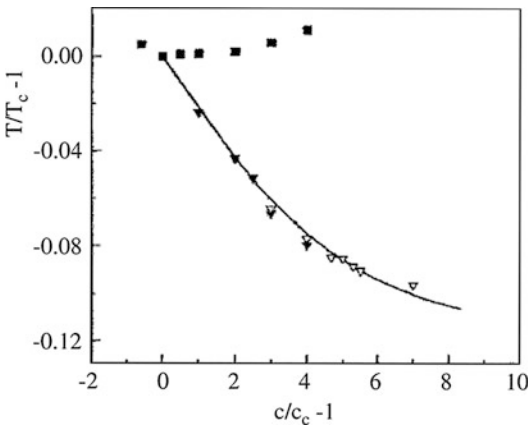
In (c), the system is made of gelatin dissolved in water + methanol; ϕ is the gelatin concentration. The broken lines are characterized by the divergence of the viscosity and correspond to the sol-gel transition. Each line represents a different value of the methanol concentration, which has been chosen in such a way that the line ends at the consolute point or, below it, in the low- or high-density phase (Fig. 6).

Correlated Percolation,

Fig. 4 The theoretical spinodal (dashed), coexistence (continuous), and percolation (dashed) lines (from top to bottom) according to the Baxter’s model compared with the experimental data in water-in-oil microemulsions (AOT/water/decane). (From Chen et al. 1994)



In all these experiments the consolute point is characterized by a thermodynamic singularity, where the correlation length and compressibility diverge. The other lines are usually ascribed to a “percolation” transition. However, it is important to precise which are the relevant clusters in the three different systems. Also, we would like to understand why, in system (c), the viscosity diverges at the percolation transition, while in (b) it reaches a plateau, and why in (a) and



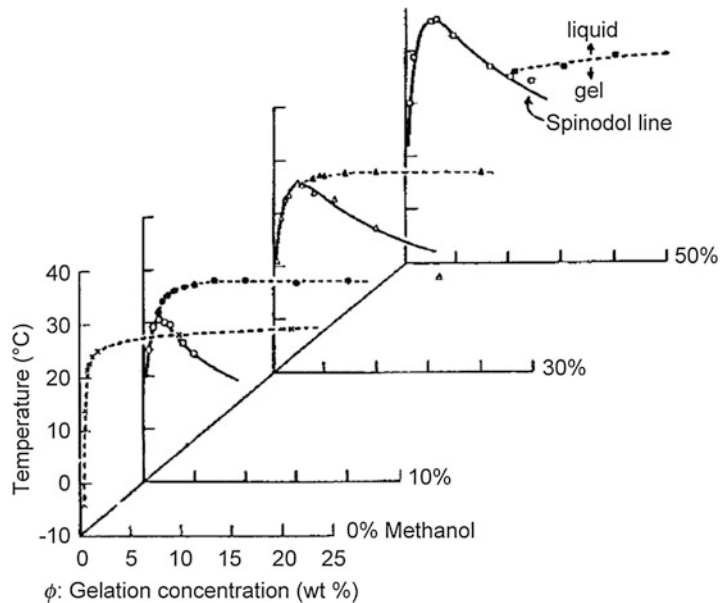
Correlated Percolation, Fig. 5 *L/64* water system. Experimental points of the coexistence curve and percolation line, where the viscosity exhibits a steep increase. (From Mallamace et al. 2000)

(b) the “percolation” lines end on the coexistence curve close to the critical point in the low-density region. It is also important to realize that for each case we need to define the proper cluster, which is responsible for the physical phenomenon. In the conductivity experiments in microemulsions the proper clusters are made of “touching” spheres similar to nearest neighbor particles in a lattice gas model. The viscoelastic properties of microemulsions may be more suitably described by clusters made of pairwise bonded spheres. For a more refined percolation model in microemulsions, see (Grest et al. 1986).

From the cluster properties of the lattice gas model we expect the infinite cluster is a necessary condition for a critical point, therefore the percolation line ends just below the critical point in the low density region, as observed in the experiments described above and more recently in numerical simulations of models of interacting colloids (Romano et al. 2007; Zaccarelli 2007).

In weak reversible gelatin the clusters are made of monomers (or polymers) bonded by strong interaction, which leads to chemical bond. In this case the bond probability can be changed by changing the solvent and therefore the percolation line, by properly choosing the solvent, can end on the coexistence curve at or below the critical point.

Correlated Percolation, Fig. 6 Sol-Gel transition temperature (solid symbols) and the spinodal temperature (open symbols) of gelatin-water-methanol mixtures as function of gelatin concentration. At the sol-gel transition, the viscosity diverges. (From Tanaka et al. 1979)



The reason why the viscosity in the gel experiments diverges at the percolation point, while it reaches a plateau in colloids, is due to the lifetime of the bonds, which is much longer in the first system than in the second (Del Gado et al. 2004; Saika-Voivod et al. 2004; Mallamace et al. 2006). In low-density colloids, the proper clusters to describe colloidal gelation also appear to be related to strong bonds with large bond lifetime (Gimel et al. 2001; Coniglio et al. 2004, 2007; de Candia et al. 2005; I et al. 2005; Saika-Voivod et al. 2004). When the relaxation time is much smaller than the bond lifetime the dynamics is dominated by the clusters, otherwise a crossover is expected towards a regime due to the crowding of the particles (Coniglio et al. 2004, 2007; de Candia et al. 2005). Percolation line of pairwise bonded clusters can also be defined in fluids, but due to the negligible lifetime cannot be detected.

Scaling Behavior of the Viscosity

If the lifetime of the chemical bonds is infinite, the viscosity exhibits a divergence at the percolation threshold as recently shown in different models (Del Gado et al. 2000; Broderix et al. 2000; Vernon et al. 2001)

$$\eta \sim \xi^{\bar{\nu}}, \quad (52)$$

where ξ is the linear dimension of the critical cluster which diverges at the percolation threshold with the exponent ν .

The relation between the diffusion coefficient $D(R)$ of a cluster of radius R and the viscosity η would be given by the Stokes–Einstein relation for a cluster radius much larger than ξ

$$D(R) \sim \frac{1}{R\eta}. \quad (53)$$

For cluster radius R smaller than ξ it has been proposed (Martin et al. 1988) that the viscosity will depend also on R in such a way to satisfy a generalized Stokes–Einstein relation Eq. (53)

with $\eta = \eta(R)$. When $R = \xi$ the viscosity $\eta(\xi) = \eta$, and from Eq. (53) one obtains the following scaling behavior for R :

$$D(R) \sim R^{-(1+\bar{\nu})} \quad (54)$$

Therefore, the relaxation time $\tau(R)$ for a cluster of radius R is

$$\tau(R) \sim R^{1+\bar{\nu}}. \quad (55)$$

If τ is the lifetime of a typical cluster, then a cluster of radius R will contribute to the viscosity if $\tau(R) < \tau$, and therefore:

$$\eta \sim \xi^{\bar{\nu}} f\left(\frac{\tau}{\xi^{1+\bar{\nu}}}\right) \sim \begin{cases} \xi^{\bar{\nu}} & \tau > \xi^{1+\bar{\nu}} \\ \frac{\bar{\nu}}{\tau^{1+\bar{\nu}}} & \tau < \xi^{1+\bar{\nu}} \end{cases} \quad (56)$$

which implies that the viscosity will exhibit a steep increase followed by a plateau. The higher is τ , the higher is the plateau.

The viscosity data on microemulsion (Fig. 5) shows indeed such a plateau, suggesting that the mechanism for the appearance of the plateau is linked to the bond lifetime, which in turn is related to the cluster relaxation time.

Future Directions

In conclusion, we have discussed the interplay between percolation line and critical point in systems where thermal correlations play an important role. The problem to define the droplets in spin models is satisfactorily solved. However, there are still some open problems. Above $d = 4$ in the Ising model, the definition of droplets presents some difficulties, probably related to the upper critical dimension for the percolation problem which is 6. This type of difficulties does not allow for trivial extensions of the arguments used in the random percolation problem, to explain the hyperscaling breakdown. Another open problem is the characterization of the thermal scaling exponent $1/\nu$, in terms of the fractal dimension of some subset of the critical droplet, as occurs in the random percolation problem.

In the last decade, the FK,CK approach has been extended to frustrated systems. Interestingly, this approach has led to a new frustrated percolation model, with unusual properties relevant to spin glasses and other glassy systems (Coniglio 2000; Coniglio et al. 1991; Machta et al. 2007). However, the precise definition of clusters, which are able to characterize the critical droplets for spin glasses, is still missing.

Although some advances have been obtained towards a droplet definition in Lennard–Jones systems (Campi et al. 2001), a general definition for continuum models of fluids still needs to be formulated.

Appendix – Random Cluster Model and Ising Droplets

In 1969, Fortuin and Kasteleyn (FK) (Kasteleyn and Fortuin 1969; Fortuin and Kasteleyn 1972) introduced a correlated bond percolation model, called random cluster model, and showed that the partition function of this percolation model was identical to the partition function of q -state Potts model. They also showed that the thermal quantities in the Potts model could be expressed in terms of connectivity properties of the random cluster model. Much later in 1980, Coniglio and Klein (1980) independently have used a different approach with the aim to define the proper droplets in the Ising model. It was only later that it was realized that the two approaches were related, although the meaning of the clusters in the two approaches is different. We will discuss these two approaches here, and show that their statistical properties are the same.

Random Cluster Model

Let us consider an Ising system of spins $S_i = \pm 1$ on a lattice with nearest-neighbor interactions and, when needed, let us assume periodic boundary conditions in both directions. All interactions have strength J and the Hamiltonian is

$$\mathcal{H}(\{S_i\}) = - \sum_{\langle i,j \rangle} J(S_i S_j - 1), \quad (57)$$

where $\{S_i\}$ represents a spin configuration and the sum is over nm spins. The main point in the FK

approach is to replace the original Ising Hamiltonian with an annealed diluted Hamiltonian

$$\mathcal{H}'(\{S_i\}) = - \sum_{\langle i,j \rangle} J'_{ij}(S_i S_j - 1), \quad (58)$$

where

$$J'_{ij} = \begin{cases} J' & \text{with probability } p \\ 0 & \text{with probability } (1-p). \end{cases} \quad (59)$$

The parameter p is chosen such that the Boltzmann factor associated to an Ising configuration of the original model coincides with the weight associated to a spin configuration of the diluted Ising model

$$\begin{aligned} e^{-\beta \mathcal{H}(\{S_i\})} &\equiv \prod_{\langle i,j \rangle} e^{\beta J(S_i S_j - 1)} \\ &= \prod_{\langle i,j \rangle} \left(p e^{\beta J'(S_i S_j - 1)} + (1-p) \right), \end{aligned} \quad (60)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and T is the temperature. In order to satisfy (60), we must have

$$e^{\beta J(S_i S_j - 1)} = p e^{\beta J'(S_i S_j - 1)} + (1-p). \quad (61)$$

We take now the limit $J' \mapsto \infty$. In such a case, $e^{\beta J'(S_i S_j - 1)}$ equals the Kronecker delta $\delta_{S_i S_j}$ and from (61) p is given by

$$p = 1 - e^{-2\beta J}. \quad (62)$$

From (60), by performing the products we can write

$$e^{-\beta \mathcal{H}(\{S_i\})} = \sum_C W_{FK}(\{S_i\}, C), \quad (63)$$

where

$$W_{FK}(\{S_i\}, C) = p^{|C|} (1-p)^{|A|} \prod_{\langle i,j \rangle \in C} \delta_{S_i S_j}. \quad (64)$$

Here C is a configuration of interactions where $|C|$ is the number of interactions of

strength $J' = \infty$ and $|A|$ the number of interactions of strength 0. $|C| + |A| = |E|$, where $|E|$ is the total number of edges in the lattice. $W_{FK}(\{S_i\}, C)$ is the statistical weight associated (a) to a spin configuration $\{S_i\}$ and (b) to a set of interactions in the diluted model where $|C|$ edges have ∞ strength interactions, while all the other edges have 0 strength interactions. The Kronecker delta indicates that two spins connected by an ∞ strength interaction must be in the same state. Therefore, the configuration C can be decomposed in clusters of parallel spins connected by infinite strength interactions.

Finally, the partition function of the Ising model Z is obtained by summing the Boltzmann factor (63), over all the spin configurations. Since each cluster in the configuration C gives a contribution of 2, we obtain:

$$\begin{aligned} Z &= \sum_{\{S_i\}} W_{FK}(\{S_i\}, C) \\ &= \sum_C p^{|C|} (1-p)^{|A|} 2^{N_C}, \end{aligned} \quad (65)$$

where N_C is the number of clusters in the configuration C .

In conclusion, in the FK formalism the partition function of the Ising model (65) is equivalent to the partition function of a correlated bond percolation model (Kasteleyn and Fortuin 1969; Fortuin and Kasteleyn 1972; Hu 1984, 1992; Hu and Mak 1989), where the weight of each bond configuration C is given by

$$W(C) = p^{|C|} (1-p)^{|A|} 2^{N_C}, \quad (66)$$

which coincides with the weight of the random percolation except for the extra factor 2^{N_C} . The correlation is due to the presence of this extra factor. Clearly all percolation quantities in this correlated bond percolation model can be obtained by using the weight given by Eq. (66). Interestingly, using (64) and (63) Fortuin and Kasteleyn have proved that (Kasteleyn and Fortuin (1969), Fortuin and Kasteleyn (1972))

$$|\langle S_i \rangle| = \langle \gamma_i^\infty \rangle_W \quad (67)$$

and

$$\langle S_i S_j \rangle = \langle \gamma_{ij} \rangle_W, \quad (68)$$

where $\langle \dots \rangle$ is the Boltzmann average of the standard Ising model (57) while $\langle \dots \rangle_W$ is the average over bond configurations in the bond correlated percolation, with weights given by (66). Here $\gamma_i^\infty(C)$ is equal to 1 if the spin at site i belongs to the spanning cluster in such bond correlated percolation, 0 otherwise; $\gamma_{ij}(C)$ is equal to 1 if the spins at sites i and j belong to the same cluster, 0 otherwise. Eqs. (67, and 68) link the connectivity properties of the correlated percolation with weights given by (66), with the Boltzmann average of thermal quantities.

Connection Between the Ising Droplets and the Random Cluster Model

In the approach followed by Coniglio and Klein (1980), given a configuration of spins, one introduces at random connecting bonds between nn parallel spins with probability p_b , antiparallel spins are never considered connected. Clusters are defined as maximal sets of parallel spins connected by bonds. The bonds here are fictitious, they are introduced only to define the clusters and do not modify the interaction energy as in the FK approach. For a given realization of bonds, we distinguish the subsets C and B of nn parallel spins, respectively, connected and not connected by bonds and the subset D of nn antiparallel spins. The union of C , B , and D coincides with the total set of nn pair of spins E . The statistical weight of a configuration of spins and bonds is (Coniglio 1990; Coniglio et al. 1989)

$$W_{CK}(\{S_i\}, C) = p_b^{|C|} (1-p_b)^{|B|} e^{-\beta \mathcal{H}(\{S_i\})}, \quad (69)$$

where $|C|$ and $|B|$ are the number of nn pairs of parallel spins respectively in the subset C and B not connected by bonds. For a given spin configuration, using Newton binomial rule, we have the following sum rule

$$\sum_C p_b^{|C|} (1 - p_b)^{|B|} = 1. \quad (70)$$

From Eq. (70) follows that the Ising partition function, Z , may be obtained by summing (69) over all bond configurations and then over all spin configurations.

$$\begin{aligned} Z &= \sum_{\{S_i\}} \sum_C W_{CK}(\{S_i\}, C) \\ &= \sum_{\{S_i\}} e^{-\beta \mathcal{H}(\{S_i\})}. \end{aligned} \quad (71)$$

The partition function of course does not depend on the value of p_b which controls the bond density. By tuning p_b instead it is possible to tune the size of the clusters. For example, by taking $p_b = 1$ the clusters would coincide with nearest neighbor parallel spins, while for $p_b = 0$ the clusters are reduced to single spins. By choosing the droplet bond probability $p_b = 1 - e^{-2\beta J} \equiv p$ and observing that $e^{-\beta \mathcal{H}(\{S_i\})} = e^{-2\beta J |D|}$, where $|D|$ is the number of antiparallel pairs of spins, the weight (69) simplifies and becomes:

$$W_{CK}(\{S_i\}, C) = p^{|C|} (1 - p)^{|A|} \prod_{\langle i, j \rangle \in C} \delta_{S_i S_j}, \quad (72)$$

where $|A| = |B| + |D| = |E| - |C|$ and the product of the Kronecker delta implies that the spin configurations are compatible with the bond configuration C . This result shows that the weights of the CK droplets coincide with the weight of the FK clusters.

From (72), by summing over all the spin configurations we can calculate the weight $W(C)$ that a given configuration of connecting bonds C between nn parallel spins occurs namely

$$\begin{aligned} W(C) &= \sum_{\{S_i\}} p^{|C|} (1 - p)^{|A|} \prod_{\langle i, j \rangle \in C} \delta_{S_i S_j} \\ &= p^{|C|} (1 - p)^{|A|} 2^{N_C}. \end{aligned} \quad (73)$$

Consequently in (71) by taking first the sum over all spins compatible with the configuration C , the partition function Z can be written as in the FK formalism (65).

$$Z = \sum_C p^{|C|} (1 - p)^{|A|} 2^{N_C}. \quad (74)$$

In spite of the strong analogies the CK clusters and the FK clusters have a different meaning. In the CK formalism the clusters are defined directly in a given configuration of the Ising model as parallel spin connected by fictitious bonds, while in the FK formalism clusters are defined in the equivalent random cluster model. However, due to the equality of the weights (72) and (64) the statistical properties of both clusters are identical (Coniglio et al. 1989) and due to the relations between (64) and (66), both coincide with those of the correlated bond percolation whose weight is given by (66). More precisely, any percolation quantity $g(C)$ which depends only on the bond configuration has the same average

$$\langle g(C) \rangle_{FK} = \langle g(C) \rangle_{CK} = \langle g(C) \rangle_W, \quad (75)$$

where $\langle \dots \rangle_{FK}$, $\langle \dots \rangle_{CK}$ are the average over spin and bond configurations with weights given by (64) and (72), respectively, and $\langle \dots \rangle_W$ is the average over bond configurations in the bond correlated percolation with weights given by (66). In view of (75) it follows (Coniglio et al. 1989)

$$\langle \gamma_i^\infty \rangle_{FK} = \langle \gamma_i^\infty \rangle_{CK} = \langle \gamma_i^\infty \rangle_W \quad (76)$$

and

$$\langle \gamma_{ij} \rangle_{FK} = \langle \gamma_{ij} \rangle_{CK} = \langle \gamma_{ij} \rangle_{CK}. \quad (77)$$

where $\langle \dots \rangle_{FK}$, $\langle \dots \rangle_{CK}$, and $\langle \dots \rangle_W$ are the average over spin and bond configurations with weights given by (64), (72), and (66), respectively. Finally, in view of (67) and (68),

$$|\langle S_i \rangle| = \langle \gamma_i^\infty \rangle_{CK} \quad (78)$$

and

$$\langle S_i S_j \rangle = \langle \gamma_{ij} \rangle_{CK}. \quad (79)$$

The results of this Appendix can be extended immediately to relate q -state Potts droplets to the random cluster model.

We conclude by noting that in order to generate an equilibrium CK droplet configuration in a computer simulation, it is enough to equilibrate a spin configuration of the Ising model and then introduce at random fictitious bonds between parallel spins with a probability given by (62).

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Principles of the Theory of Continuum Percolation

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Article Outline

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Introduction

Percolation theory is concerned with the variations of the properties of a system that is made of members when the amount of connections between the members increases. As is already apparent from that concern, the theoretical predictions for these variations are determined by the basic (or the local) definition of the connection between two members in the system. It turns out that this basic problem is relevant to many areas of science and numerous systems, from as small as nuclear matter (Satz and Fortunato 2001) to as large as galaxies (Schrijver et al. 1992). In between those two extremes, the abovementioned behavior is of interest in science, technology, engineering and their applications. This is in numerous composites (Vionnet-Menot et al. 2005), porous media (Hunt and Ewing 2009), microemulsions (Cametti et al. 1990), disordered semiconductors (Shklovskii and Efros 1984), disordered superconductors (Octavio et al. 1988), molecular (Heyes and Melrose 1998) and macromolecular (Chatterjee 2000) liquids, nano-tubes in composites (Dalmas et al. 2006) and suspensions (Foygell et al. 2001), quantum dot composites (Balberg et al. 2007), thin metal films (Song et al. 1992), layered materials (Day et al. 2003),

quasi-crystals (Rapp et al. 2005), chemical networks (Pagnotta et al. 2005) and transport in them (Planes et al. 1998), biological networks (Wille et al. 2006) and flow in them (Sokolowska et al. 2004), bioinformatics (Re et al. 2006), and ecological systems (Williams and Snyder 2005). Then there are the properties associated with the flow of charge carriers, such as electrical conductivity (Balberg 1987a), the flow of liquids such as the permeability (Murat et al. 1986), as well as corresponding processes such as displacements (Wilkinson 1986), drainage (Andrade et al. 2000), dispersion (Sahimi and Imdakm 1988), hydrological flows (Berkowitz and Balberg 1992), and diffusion (Wagner and Balberg 1987). Very closely related is the class of rheological properties (Du et al. 2004) such as the viscosity (Lin and Chen 1999). The possible variation in the local (“bond strength”) parameters makes the concepts of percolation applicable also to information and traffic management (Wu et al. 2006; Cohen and Havlin 2010). Finally, there are the related areas of elastic (Knite et al. 2002), dielectric (Grannan et al. 1981), and magnetic (Stinchcombe 1976) properties as well as their relation to electrical properties (Bergman 2003; Mandal et al. 1997; Park et al. 2004).

Before we start with their theoretical expression let us make the general concepts of local and global connectivities more concrete and intuitive, by considering an example that, while being very simple, still presents the deep core of percolation theory. In this example, we imagine a field of flowers such that each of them is surrounded, *on the average*, by Z flowers in the nearest circle of its neighbor flowers. Now we assume that the probability that a flower carries nectar is p_s . A bee can hop *only between nearest neighbor flowers* but it would like to hop only from one flower with nectar to another flower with nectar, without “wasting time and effort” in flowers that have no nectar. The probability that such a connection between two nearest-neighbors nectar-carrying flowers exists is then $p_b = p_s^2$. Hence p_b is also the probability, from the bee’s point of view, for a desirable local connection in its

journey. We thus call p_s the site percolation probability and p_b the bond percolation probability.

The question that arises then is how far can the bee travel along a route of only nectar containing flowers, given those Z and p_b ? The expected quantity to consider is $B_b = Zp_b$ which is the average number of local routes that are available (on the average) for a hop between the nectar-carrying flowers. Obviously, the larger the Zp_b product, the longer will be the possible path that it can travel. In particular, it is obvious that for a given Z , if $p_b \rightarrow 1$ the bee can travel to infinity and if $p_b \rightarrow 0$ it can travel a very short distance. The next question that arises is, what is the *smallest* value of p_b , that we denote here by p_{bc} , under which there is an infinite long path that the bee can travel? This p_{bc} is known as the percolation threshold of the system. Correspondingly, the quantity $B_{bc} = Zp_{bc}$ is known as the minimal (or critical) number of local bond-jumps per site that the bee can take in order to continue its travel to “approximate invariant.” This B_{bc} turns to be a topological dimensional (D) invariant that has a value of 2 for $D = 2$ and 1.5 for $D = 3$ (Ziman 1979). Two simple useful examples are the $Z = 4$ case (as in a square lattice) which yields that $p_{bc} = 1/2$ and the $Z = 6$ case (as in a cubic lattice) which yields that $p_{bc} = 1/4$. The mentioned dimensional invariance B_{bc} can be understood intuitively since for the formation of such an infinite path, the higher the local Z , the smaller the probability p_{bc} that is needed in order for a single bond to form along the above path, and thus to increase the probability of an infinite path of connected bonds to exist. A consequence of that is also that the higher the dimensionality, the smaller the B_{bc} . This can be appreciated by the fact that for very high dimensions, just a little more than $B = 1$ is needed to form an infinite path (Wagner et al. 2006). One notes here that the path “drawn” by the bonds can be very tortuous, the smaller the p_b in the interval $1 > p_b > p_{bc}$, the more tortuous this path.

The next question that arises in the above scenario of flying bees is how far can the bee travel for a given p_b in the interval $0 < p_b < p_{bc}$ (i.e., for a p_b that does not provide an infinite path)? Noting that p_{bc} is the only specific information that we have on the system the question can be rephrased as, what is the dependence of the finite travel length ξ of the

bee (or hereafter the correlation length (Stauffer and Aharony 1992)) on that p_{bc} ? Not less interesting is the question, how does that ξ “jump” from a finite travel distance (for p_b in the above interval) to its infinite length as $p_b \rightarrow p_{bc}$. The reasonable way to guess the latter behavior is to assume that the transition in ξ will simply depend on the proximity of p_b to p_{bc} . On the other hand, since ξ diverges as $p_b \rightarrow p_{bc}$ the simplest option to describe the p_b dependence of ξ is by using the inverse proportionality, that is, $\xi \propto 1/(p_{bc} - p_b)$. Hence, noting the behavior of diverging quantities in the theory of phase transitions, one would expect that a more rigorous and exact theory will yield a relation such as $\xi \propto (p_{bc} - p_b)^{-\nu}$ (or $\xi \propto (B_{bc} - B_b)^{-\nu}$), where ν is some exponent that can be derived from that theory. For example, such a diverging “correlation lengths” ξ are typical of phase transitions in general, and in the ferromagnetic to paramagnetic transition, where spin aligned clusters of diameter ξ are formed, in particular. The typical variable parameter that changes the value of ξ there is the temperature, and correspondingly, there exists there a critical temperature (Stanley 1971). Indeed, the mapping of the percolation model onto models of magnetic transition has enabled the determination of corresponding critical exponents such as ν (Fortuin and Kasteleyn 1972). Intuitively, this is also not unexpected from the site percolation point of view since the percolation “occupation” probability p_s can be taken as the probability for (say) a spin up and the $1 - p_s$ non-occupation probability as the probability of a spin down in the system. In this review we will be concerned then with the above two basic features of percolation theory, that is, the percolation threshold and the critical behavior.

Historically, percolation theory was developed in the second half of the twentieth century using lattice models. The members of the systems such as the lattice basic segments (or the edges of the unit cell) were taken as the bonds while the nodes of the lattice (or the corners of the unit cell) were taken as the sites of the lattice. In our above story on the bees, the nectar-carrying flowers are the occupied sites and the corresponding p_b is the probability of the bee’s hop. From there, the question that have been asked in the percolation problem are essentially the ones considered above. These are, what is the percolation threshold, that

is, what is the probability of the locally available bonds or sites at which global connectivity is established, and how do the geometrical and physical properties of the system change with the variation of those probabilities?

Noting that percolation behaviors exist in many natural and artificial systems that can or cannot be accounted for by the theory of lattice percolation, required then a build-up of a theory that will provide such corresponding accounts. On the other hand, the great strides that were made in the theory of lattice percolation have made the basic nomenclature and the formalism rely on the basis that was developed for the lattices. Here, we call all those “off lattice” systems, continuum systems, and accordingly, we use the term continuum percolation theory to describe the collection of problems associated with the properties of those systems. The recognition of the importance of that theory and the very wide range of practical applications that it brought, since the last quarter of the twentieth century, have prompted numerous research works and many applications in all the fields that were mentioned above.

To set our description on a firm theoretical basis we will first review the basic understanding that was achieved in the theory of lattice percolation and then turn to the continuum systems. However, since there are so many classes of those we will focus mostly on one of them with the hope that one can extend its understanding to that of the other continuum percolation systems that one may encounter. To appreciate the added complexity in continuum percolation we can consider a corresponding system of objects where one can define a local connectivity criterion such as the overlap of pores in porous media. The objects are assumed to be randomly distributed in space, and they may have various and even variable shapes and sizes, as well as interactions with each other. The difficulty in dealing with such a system is apparent already from the ambiguity in defining the local connectivity. For example, if there is a partial overlap of such pores are they connected or not and how? Indeed, we will discuss that problem which has no counterpart in lattice percolation.

Following the above and the limited length of this review, we start our discussion in section

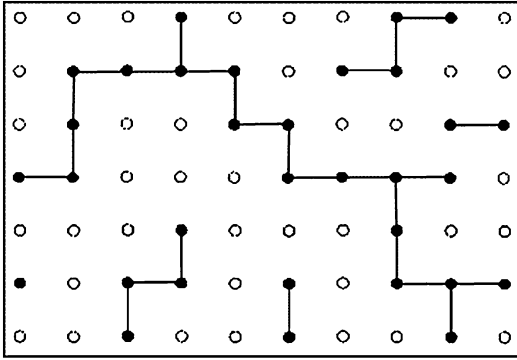
“[Percolation in the Lattice](#)” with a short review of lattice percolation theory in order to present the essence and the nomenclature of that theory. Then we turn to a longer account that is concerned with the main subject of this review, that is, the continuum case. This is done in order to enable the more experienced reader to skip some topics of section “[Percolation in the Lattice](#)” before he/she turns to section “[Between Lattice and Continuum Percolation](#),” which is putting the bridge between the formally developed lattice percolation theory and the more recently developed theory of continuum percolation. Section “[Percolation in the Continuum](#)” is then the central part of this review, which provides the basics of continuum percolation theory as well as some more recent developments and additional concepts that were introduced in that theory.

Each of our sections is divided to few subsections. They are devoted to the threshold, the critical behavior in general, and the critical behavior of the electrical conductivity in particular. The latter is probably the most studied property of percolation theory and it is the most conspicuous one concerning its applications. We dwell on the theory of the latter property since it encompasses the basics of continuum percolation for systems that cannot be accounted for by the lattice percolation theory. In passing, we remark that due to the limited scope of this review we will try to present the main ideas and their model manifestations, noting that numerous computer simulations have confirmed all of the conclusions reached here, while only very few of them will be mentioned here. On the other hand, to connect the conclusion of the theory to the “real world,” being a central task of the theory of percolation in the continuum, we will mention in each subsection the relevant experimental results that were confirmed, or were accounted for, by the relevant theoretical predictions.

Percolation in the Lattice

The Percolation Thresholds

To introduce the abovementioned basic concepts we start by considering the very simple model of the two-dimensional square lattice that is illustrated in Fig. 1.



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Fig. 1 An illustration of a portion of an infinite two-dimensional lattice. The open circles represent the unoccupied lattice sites and the full circles represent occupied lattice sites. The segments connecting two nearest neighbor occupied sites represent a local connection or an occupied bond. In this illustration, there are finite clusters of connected sites (of “size” 1, 2, and 4) and a “spanning” cluster that connects two opposite edges of the system. In a system of infinite “size,” the latter is known as the “infinite” or the “percolation” or the spanning cluster. (From Berkowitz and Balberg 1993)

Let us assume a probability, p_s , that a lattice site is occupied, and denote the occupied sites by full circles. The step that is very important here, and will be very basic when we discuss continuum percolation, is the definition of the local connectivity between members in a given system. In the present lattice, these members are the occupied sites. Two such occupied sites are defined to be connected if they are first nearest neighbors. In the particular case shown in Fig. 1 the number of nearest neighbors of a given site (the coordination number of the lattice), Z , is 4. We can now define a connected cluster as a group of sites such that each of them is connected to at least one other occupied site in this group. The size of the cluster is defined as the number of the sites in it. In Fig. 1 we see then clusters of size 1, size 2, size 4 and a larger “spanning” cluster that connects opposite edges of the system. In percolation theory, we are concerned mainly with “infinite” systems, that is, with systems where the details, for example, the sites themselves and the inter-site distances (lattice-segments, or unit cell edges, or bonds) are much smaller than the size of the system. Correspondingly, in an “infinite” system we call the spanning

cluster, the percolation cluster, or the infinite, cluster. The illustration given in Fig. 1 reflects, however, only a small (finite) portion of the infinite system. Such small portions are used below for the description and definitions of local and global quantities of the system, but it has to be remembered that quantitative characterizations of its various properties are considered meaningful only in the (statistically sufficient) “infinite” system limit.

From Fig. 1 it is easy to appreciate that the number of clusters and their sizes will vary as the site occupation probability, p_s , increases, as can be derived quantitatively by various models and simulations (Stauffer and Aharony 1992; Zallen 1983). The most important consequence, however, is that there will be a value of p_s that is known in the literature as the sites percolation threshold p_{sc} , such that for $p_s < p_{sc}$ there is no spanning cluster, while for $p_s \geq p_{sc}$ there is such a cluster. The dependence of the various geometrical or physical properties on p_s in the close proximity of p_{sc} is known as the critical behavior. The analysis of the properties of lattices such as in Fig. 1 is usually referred to as the site percolation problem. In complete analogy, one can consider the line segments in Fig. 1 as the system’s members that may or may not be connected. These lattice segments (or lattice spacing) are usually referred to as bonds, and then, if they connect two occupied nearest neighbor sites, they are called occupied bonds while otherwise they are referred to as unoccupied bonds. Two bonds are considered connected if they have a common site. In that case, the bond occupation probability, p_b , determines the corresponding connectivity and the behavior of the percolation properties of the system. The corresponding analysis is known then as the bond percolation problem. For lattices, however, the relation $p_b = p_s^2$ applies in any dimension as can be proven rigorously (Balberg 2017) and appreciated intuitively (Shakland and Waff 1974; Kirkpatrick 1973), simply from the fact that for (a lattice-spacing) bond to be occupied, its two end-sites must be occupied. This

$$p_b = p_s^2 \quad (1)$$

relation yields that, if we only know p_s or p_b (Balberg 2017), we also know the other one.

To consider the above picture more generally we examine a lattice where the number of the j th nearest neighbors per site is z_j , and the “total” number of its neighbors, up to and including the n th neighbor, is $Z_n = \sum z_j$. Let us evaluate now the connectivity of the system when we assume that only the first n nearest neighbors are involved. The random occupation of the bonds with a probability p_b yields that the average number of occupied bonds, of the j th neighbors per site, is $p_b z_j$. Correspondingly, the total average number of occupied bonds per site, including all the occupied bonds that are associated with the first n nearest neighbors, is $p_b Z_n$. The dependence of the percolation threshold on Z_n follows simply the topological requirement that, for a given dimension, there is a universal number of bonds per site B_{bc} that is needed for the onset of a percolation cluster. It turns out that topologically, B_{bc} is a dimensional invariant being 2 for $D = 2$ and 1.5 for $D = 3$ (Ziman 1979). The necessary probability for the bonds to be occupied, in order to achieve the onset of percolation, is then (Balberg et al. 2013).

$$p_{bnc} = B_{bc}/Z_n. \quad (2)$$

We note in passing that in the classical percolation theory one usually considers only the $n = 1$ case (Stauffer and Aharony 1992). Following the increase of Z_n with $n > 1$ (i.e., the involvement of farther neighbors in the lattice), it is obvious that a corresponding series of percolation thresholds, p_{bnc} , can be obtained and that $p_{bnc} < p_{b(n-1)c}$. The above considerations apply also to the site percolation problem since the involvement of more participating bonds will yield a larger number of occupied sites. Hence, we have that the corresponding percolation thresholds in the latter case, that we denote here by the p_{snc} values, will also obey the rule that $p_{snc} < p_{s(n-1)c}$ (Balberg et al. 2013). Of course, p_{s1c} corresponds to the classical, first nearest neighbor, site-percolation problem and (for the convenience of the following discussion) we define here p_{s0c} as 1. For reasons that will come apparent in section “The Percolation Behavior of the Electrical Conductivity” we call the effects associated with those thresholds the staircase behaviors.

Experimental Confirmations and/or Explanations of Experimental Results

While numerous simulations have determined the percolation thresholds in lattices only very few analytic expressions (Stauffer and Aharony 1992) or approximations (Godowsky 2000) were derived for them. On the experimental end, the first confirmation of the lattice p_{sc} value was given by Adler et al. (1973). They have constructed a cubic lattice where the nearest neighbor occupied bonds were made of resistors. The onset of electrical conductivity was at $p_{sc} = 0.33$ which is in excellent agreement with the simulation results and analytic expectations (Stauffer and Aharony 1992; Zallen 1983).

The Critical Behavior of Percolation Clusters

Various properties of “percolating” systems are expected to exhibit power-law dependencies such as in phase transitions, the most rigorous of which is the Ising model of magnetic systems (Stanley 1971). In that lattice model, where each atom has an up or down spin, the energy required to align the spins of two neighboring atoms requires an interaction energy J . Assuming an equilibrium Boltzmann statistics, the probability of neighboring atoms to have the same spin is determined by $1 - \exp(-J/kT)$, where kT is the thermal energy. We can also look at this probability as the one for the two nearest neighbors to be bonded (Stauffer and Aharony 1992). In percolation theory this probability is the bond occupation probability p_b . This is the core for the mapping of the percolation theory onto the theory of phase transitions (Fortuin and Kasteleyn 1972; Potts 1952; Essam 1979; Wu 1978, 1982). In particular, the size of magnetically aligned clusters in magnetic systems and the size of clusters of connected bonds in “percolating” systems can be shown to exhibit the same behaviors. Correspondingly, the average size of the percolation clusters will diverge at some p_{bc} and the global magnetization will be set at some T_c . This suggests that the critical dependence on $p_{bc} - p_b$ (for $p_b < p_{bc}$) is analogous to the $T - T_c$ dependence (for $T > T_c$), as in both cases only finite size connected clusters will exist and the corresponding properties will diverge at those critical quantities (Stauffer and

Aharony 1992). All that was formally proven by the magnetic Potts model (Potts 1952) which is a formal generalization of the Ising model for systems where the spins can have many orientations (rather than the Ising $q = 2$ model) and in particular q can even have non-integer values (Potts 1952; Essam 1979; Wu 1978, 1982). This enables the solution of the (percolation related) $q \rightarrow 1$ limit as well as the considerations of a diminishing external magnetic field, which enables then to exclude the “magnetic” effects of the Ising model and to leave only the connectivity effects. That procedure provided the rigorous theoretical basis for percolation theory. For the purpose of this review, it is sufficient to consider the phase transition behavior of the percolation properties (Stauffer and Aharony 1992) and to know that this behavior was rigorously proven (Wu 1978, 1982). Recalling Eq. (1) shows that the same conclusions apply to the site percolation problem (Balberg 2017).

The abovementioned considerations of the percolation as a phase transition yield then that percolation affected properties will be well described by power laws of the proximity to the threshold $p_d = |p - p_c|/p_c$. *Here, we use p generically when the discussion applies to both sites and bonds.* Starting with the average cluster size, S , that is defined usually (Stauffer and Aharony 1992) as the average number of sites or bonds in a cluster, per an occupied site, or an occupied bond in the lattice, one has then that for clusters of finite size in the lattice, whether, $p > p_c$ or $p < p_c$

$$S \propto |p - p_c|^{-\gamma}. \quad (3)$$

In particular, the phase transition-like behavior yields that exponents, such as γ , depend only on the lattice dimension D , and are thus independent of the details (e.g., the lattice type) of the system. This property is known as universality and the corresponding dependence on $|p - p_c|$ as the universal behavior. For example, the universal values of γ are 2.4 for $D = 2$ and 1.8 for $D = 3$. The other major property of the clusters is their spatial-geometrical extent, ξ , which can be defined as their effective (e.g., gyration) radius (say, in units of the lattice spacing) (Stauffer and Aharony

1992). As to be expected from the above discussion (and section “Introduction”), this length behaves as

$$\xi \propto |p - p_c|^{-\nu}, \quad (4)$$

where ν is the corresponding “universal” exponent. The quantity ξ , known also as the correlation length, is, as in other phase transitions, the most important parameter of the system since it characterizes its connectivity and provides the basic length scale for dealing with the behavior of percolation related properties in the system. The well-known values of ν are 1.33 for $D = 2$ and 0.88 for $D = 3$ (Stauffer and Aharony 1992; Zallen 1983).

Considering Eq. (4) it is apparent that ξ can become infinite as p approaches p_c . This means that there is a cluster of occupied bonds (or sites) that has an infinite extent. To characterize the “size” of this cluster one defines the cluster percolation probability P , for $p > p_c$, as the probability of a given bond (or site) to belong to this infinite (or spanning) cluster. Following the above analogs of percolation and the magnetization in a ferromagnet, P is given by the power law (Stauffer and Aharony 1992; Wu 1978)

$$P \propto (p - p_c)^\beta, \quad (5)$$

where β is defined as the percolation cluster exponent (Balberg and Binenbaum 1985). An important portion of the above-defined percolation cluster is the collection of all its members such that each of them is connected through occupied bonds (or sites) to any of the far (infinite) opposite edges of the sample, without going through the same bond, or site, twice (see more in the next subsection). Obviously, dangling bonds or dangling clusters of bonds (i.e., clusters that have only a single common site with the rest of the percolation cluster) are not included in this sub-cluster. This collection of bonds (or sites) is known as the backbone of the percolation cluster or the backbone of the system (Sahimi 1984; Bunde and Havlin 1991). As the other quantities above, the probability of a bond (or a site) to belong to this backbone $B_B(p)$ is given by

$$B_B(p) \propto (p - p_c)^{\beta_B}, \quad (6)$$

with the corresponding exponent β_B (Stauffer and Aharony 1992; Sahimi 1984; Bunde and Havlin 1991). We remark then that the details of the system are not important for all the above properties and that it is only the global connectivity of those properties that determines the abovementioned behaviors. This is of course the reason that the particular lattice type concerned and the local connectivity involved (e.g., the value of Z) are of no importance for the critical behaviors that are exhibited by Eqs. (2), (3), (4), (5), and (6). In passing, we note that other properties of the system, such as the ratios between the amplitudes of the above properties, have been also found to be universal for lattices (Aharony 1980; Mertens et al. 2017; Lee 1996), but in this review we concentrate only on the exponents that characterize the critical behavior.

We recall here that in phase transitions, the critical $p - p_c$ asymptotic behavior takes place in the vicinity of p_c and the question that arises then is, how wide is the asymptotic regime in which the above critical exponents will be observed? To approach this problem we have to have a scale to measure this width. One can immediately see that the difference $p - p_c$ does not provide useful information in that regard. This is since if p_c is relatively large (in the $p_c < p < 1$ interval) the variation in the connectivity between p_c and p is relatively small while when for the same $p - p_c$, $p_c \rightarrow 0$, the variation of the connectivity is relatively large. Being interested in a large variation of the connectivity (and the corresponding length ξ of Eq. (4)), that is, with the critical behavior of the system, requires a more meaningful, p to p_c , proximity parameter. Having as information only the value of p_c , if we choose $(p - p_c)/p_c$ as the scaling parameter the effect of a large variation of the connectivity (i.e., of ξ) is well represented. Indeed, the need to use this scale was shown rigorously (Kaliski and Cohen 2006) and some authors did use it in the presentation of their simulation results (Kebblinski and Cleri 2004). Correspondingly, the more useful parameter to characterize the proximity of p to p_c is the normalized quantity (Balberg 2017):

$$p_d = (p - p_c)/p_c. \quad (7)$$

Considering the fact that the largest p is 1 and that in the smallest p_c in 3D is ~ 0.1 for the bond percolation system and ~ 0.2 for the site percolation, this p_d cannot be very large. However, as will be mentioned latter (see section “Further Extensions for Various Off-Universal Conductivity Exponents in Continuum Systems”), this is not the case for off-lattice systems (Balberg 2017).

Turning to the other extreme, that is, when $p \rightarrow 1$, the finite clusters are small and the global properties of the system are determined by the infinite cluster that actually fills the system. Hence, the above percolation approach for the derivation of the system properties as a function of p , being insensitive to the connectivity of the system, is clearly inappropriate. The method used to describe the system then is to consider some global averages that are practically taken in the $p \rightarrow 1$ case, by assigning to each and all the local bonds (whether occupied or not) an effective value of this property that is different than the value that was originally assigned to the occupied bonds. This method, known as the effective medium approximation (EMA), is of particular use for the determination of the electrical conductivity of systems, such as those that will be mentioned in next subsection (Kirkpatrick 1973; Sahimi 2003). We note, however, that in the EMA one obtains dependencies of various properties on $p - p_c$, but both the values of p_c and the corresponding exponents, are different from those of percolation theory. Of course with the increase of p from p_c toward $p = 1$ there is a smooth continuous transition from that of the critical percolation behavior to that of the effective medium behavior (Kirkpatrick 1973).

Experimental Confirmations and/or Explanations of Experimental Results

Here we note that exact values of the percolation exponents were derived thus far analytically only for two-dimensional lattices and those were from the application of renormalization group calculations (Bunde and Havlin 1991; Sahimi 2003). On the other hand, the determination of the clusters’ geometrical exponents in lattices is almost

exclusively done by simulations (Stauffer and Aharony 1992). The easiest and most common experimental tool for checking the behavior of percolation theory regarding the critical behavior is (as detailed below) the measurement of electrical conductivity. At the experimental end we can mention the conspicuous work of Liu and Regenauer-Leib (2011) that derived the correlation length exponent (ν) in lattices by a computer-controlled experiment.

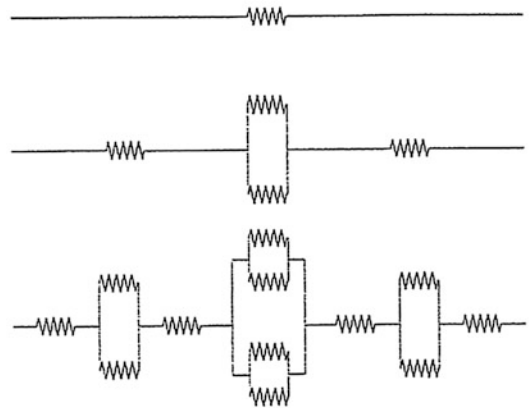
The Percolation Behavior of the Electrical Conductivity

Turning from the above geometrical-statistical properties to the dynamical properties associated with the connectivity of the system in lattices, we consider the global conductance of a system, G . To do that let us view the system shown in Fig. 1 as consisting of “bonds” (between two occupied sites), where each bond is a resistor with a given resistance value. In such a system, there will be electrical conduction from right to left or from top to bottom, only if there is a spanning cluster. Examining that system, we see that only a fraction (15 from left to right or 11 from top to bottom) of the 18 bond-resistors in this cluster would participate in the electrical conduction process in the respective (voltage induced) direction. On the other hand, there will be a few resistance bonds (here 3 in the left to right direction and 7 in the top to bottom direction) that do not participate in the conduction processes. However, of the illustrated “spanning” cluster 17 bonds can participate in the possible conduction process while there is a single bond that cannot participate in that process. We define then the bonds of the first type as belonging to the backbone of the percolation cluster while the other type of bonds as “dead ends” or “dangling bonds” of the percolation cluster. In the more general case, according to our definition, if there are closed loops of bonds (or resistors) that are connected only by one site (or resistor’s end) to the percolation cluster (as can be also appreciated electrically), they are not included in the backbone. In Fig. 1 we also see that in the backbone there are occupied sites with three occupied site-neighbors that form T-like junctions. These are

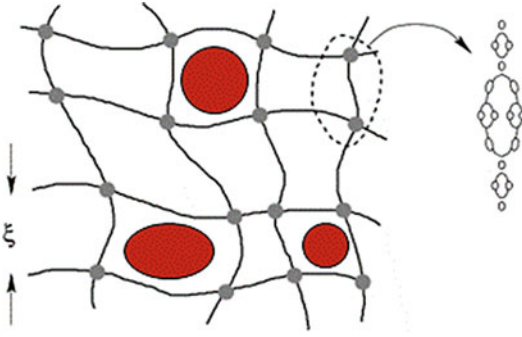
usually called the nodes of the backbone. The parts of the backbone between two neighboring nodes are known as the links of the backbone. A more general form of a segment of a backbone link (such as shown in Fig. 1) can be represented by the models of Fig. 2.

Let us consider now the structure of a more global portion of the backbone net. We can imagine the backbone as, say, a cubic net of “links” and “nodes.” Typical links can be modeled by the resistor strings, such as those shown in Fig. 2, which form a network of links that cross each other at nodes. This is because in an infinite lattice there must be many left-right and up-down infinite connecting strings as in Fig. 2. Such a portion of the backbone is illustrated in Fig. 3.

In short, the “links” intersect at the “nodes” that define the corresponding net. The entire backbone can be envisioned as consisting of, say, a topologically equivalent square or a cubic network of “links.” The links consist of a series connection of singly connected bonds and “blobs” (where the bonds form parallel connections). The average length of the links is easily appreciated to be of the order of ξ since the “holes” in the backbone net can encapsulate only finite clusters (the red entities in the figure), and those, as we saw above, have, on the average, a diameter ξ . Recalling our geometrical definition of the backbone one can appreciate



Principles of the Theory of Continuum Percolation, Fig. 2 Possible resistors models of parts of a link of a backbone. The bonds that have no parallel are called singly connected bonds and a group of bonds connected in parallel is known as a “blob” in the backbone link



Principles of the Theory of Continuum Percolation,

Fig. 3 A schematic of a larger portion of the backbone in the lattice. Also shown (on the right), a typical simple model that was used for the description of the links. The red inclusions in the figure represent the single isolated finite clusters that can reside within the “holes” in the backbone net. The average diameter of those is ξ (see Eq. (4)) and thus the average link’s length must be ξ

that Fig. 3 accounts for that definition by simply noting that from each point in that network one can reach, by “going” in opposite directions, different edges of the system. The model described here is known then as the links-nodes-blobs (LNB) model (Shklovskii and Efros 1984; Stauffer and Aharony 1992; Berkowitz and Balberg 1993). From the electrical point of view, the two singly connected bonds are simply those that carry the same current as the link and each bond-resistor in the blobs carries a smaller current than that.

Considering now the expected resistance of a cubic (or hypercubic) LNB network, let us assume that for a given p_b the resistance of a link is R_ξ . If the sample size is L we have then, on the average, L/ξ links that connect one edge of the sample with its counterpart. Correspondingly, there will be $(L/\xi)^{D-1}$ parallel links between these “opposite-edges,” where D is the dimensionality of the system. Since the link’s resistance is R_ξ , the resistance of the whole backbone network (and thus of the sample) R_L will be given by

$$R_L = R_\xi (\xi/L)^{D-2} \quad (8)$$

The crucial step left is then “only” to estimate the value of R_ξ (Shklovskii and Efros 1984; Berkowitz and Balberg 1993). The corresponding easiest approach (that can be termed also the

universal or the lattice approach) is to assume that all the occupied bond-resistors have the same resistance value r_0 (Stauffer and Aharony 1992; Bunde and Havlin 1991). In passing, we remark that the deviation from the simple single r_0 value assumption that is used in lattice models will be shown in section “Percolation in the Continuum” to lead to the very different and rich behaviors in continuum percolation systems. However, with the above assumption of all resistors having the same value r_0 , we can estimate the value of R_ξ in the LNB model as follows. We saw that the link consists of singly connected bonds and blobs. Let us determine first, how many singly connected bonds we expect to be present in a link of length ξ ? Assuming a lattice with $p_b > p_{bc}$ and assuming that there are L_1 such bonds in this link (Shklovskii and Efros 1984) we can “cut out” $(p_b - p_{bc})/p_b$ of the bonds in the whole lattice. The number of singly connected bonds that will be cut in a link will be then $L_1(p_b - p_{bc})/p_b$. If, upon the decrease of $p_b - p_{bc}$ this quantity reaches unity, there will be on the average, one singly connected bond missing in a link and “all” the links will not conduct. In the limit of $\xi \rightarrow \infty$ (i.e., $(p_b - p_{bc})/p_b < 1$) we approach then the onset of “no percolation” when $L_1 \propto (p_b - p_{bc})^{-1}$. If we neglect the blobs (that, following the above, are aggregates of parallel resistors and thus have lower resistance than the same length chain of singly connected resistors), the resistance of the link can be estimated by its lower bound of $R_\xi = r_0 L_1 \propto (p_b - p_{bc})^{-1}$. Since the blobs do contribute to the resistance of the link, one expects that $R_\xi > r_0 L_1$ and that R_ξ will behave as $(p_b - p_{bc})^{-\zeta}$ where ζ is an exponent that is dimensional-dependent. While the calculation of the value of ζ is not straightforward (Bunde and Havlin 1991), it can be well approximated by fractal models (de Arcangelis et al. 1985). However, while the value of ζ is larger than unity, it cannot be much larger than that. This is since, with the “dilution” of the network of links (as $p_b \rightarrow p_{bc}$), there is also a dilution in the local structure of the blobs, and the links will approach the limit that is not far off from a chain of singly connected bonds. In other words as $p_b \rightarrow p_{bc}$ the global resistance R_L will be affected by both the

dilution of the links in the network (Eq. (4)) and the dilution of the resistors in the blobs. The latter effect means a “stronger” (in comparison with the one that would be encountered in a link that is made only of “singly connected bonds”) divergence of the sample resistance as $p_b \rightarrow p_{bc}$ and thus it is manifested for $D < 6$, by $\zeta > 1$. Indeed, it was found that $\zeta \approx 1.3$ for $D = 2$ and $\zeta \approx 1.1$ for $D = 3$ (Stauffer and Aharony 1992; Bunde and Havlin 1991). All the above results can be summarized now by presenting the critical behavior of the global resistance, $\mathbf{R}_L$ in a percolation system of size L , by

$$\mathbf{R}_L (\equiv 1/G) \propto \mathbf{r}_0 (p_b - p_{bc})^{-t}, \quad (9)$$

where t is the critical exponent of the global conductance G , that is given, in view of the above, by

$$t_{un} = (D - 2)v + \zeta. \quad (10)$$

The t values that were derived by various corresponding analytical approximations, or Monte Carlo simulations, are known as the universal values of the universal conductivity exponent, t_{un} . These values are, in particular (Stauffer and Aharony 1992; Zallen 1983; Bunde and Havlin 1991), ≈ 1.3 for $D = 2$ and ≈ 2 for $D = 3$. Here we point out that from Fig. 3 one can appreciate intuitively that the global topology of the site percolation network is the same as that of the bond percolation network. This is another manifestation of the universality derived above in section “The Critical Behavior of Percolation Clusters.”

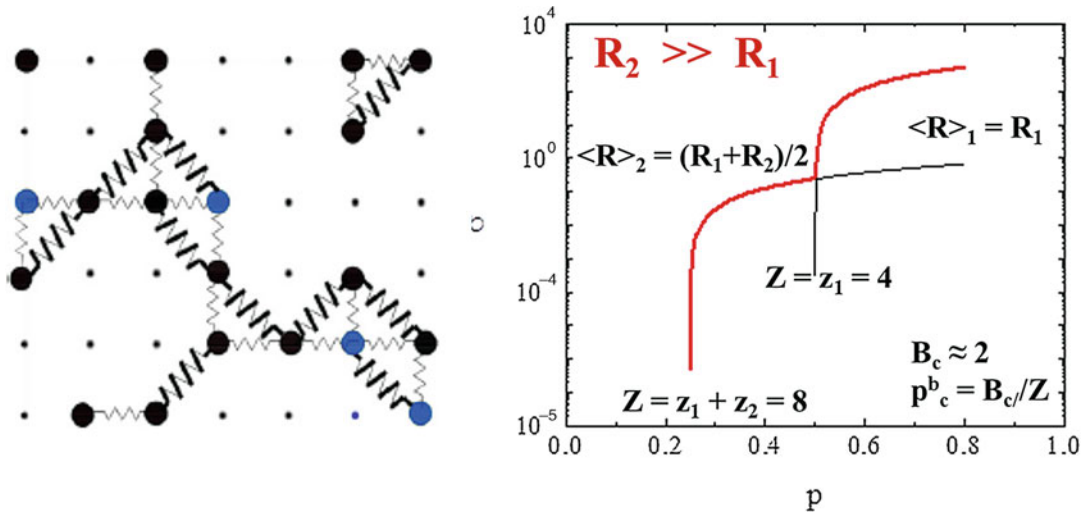
Experimental Confirmations and/or Explanations of Experimental Results

During the years, while there were numerous computational confirmations of the universal behavior of the conductivity on lattices there were only very few experimental confirmations of the predictions of Eq. (10) for lattices. Of these, probably the oldest, the most direct and the first one to determine the critical exponent in a lattice was that of Adler et al. (1973). They found for a cubic network of resistors the predicted $t \approx 2$ value.

The Staircase Model of the Conductivity In the above classical LNB model (as in many other lattice percolation models) only the resistance of the bonds between the first nearest neighbors has been considered. However, one can extend those considerations to assume farther neighbors. In particular, since the farther the neighbor the larger the distance between the corresponding neighbors, the simplest model will be to assume that the farther the neighbor the larger the corresponding resistance. Now, as we saw in section “The Percolation Thresholds” above, since $p_{bc} = B_{bc}/Z_n$, the percolation thresholds will decrease with the involvement of more of the connected neighbors (Zallen 1983). On the other hand, the larger the number of neighbors involved the larger the crucial resistances that must be involved in the conduction and these are associated with the larger resistance of the farther neighbors. The outcome of that is that the large resistors will dominate the electrical conduction at low p values and the smaller resistors will dominate the electrical conductance at the higher p values. Hence, a staircase of the conductivity, such as the one illustrated in Fig. 4, will be obtained. In the left panel of this figure, we consider a simple square lattice where the nearest neighbor bonds have a resistance R_1 and the second nearest neighbors have a resistance R_2 . The percolation threshold of solely the R_1 resistors is $p_{bc1} = B_{bc}/Z_1 (= 2/4)$ and the one that involves both the R_1 s and the R_2 s is $p_{bc2} = B_{bc}/(Z_1 + Z_2) (= 2/8)$. Assuming that $R_1 < R_2$ we get a sequence of two conductivity stairs that will vary along the stairs as $[2/(R_1 + R_2)](p_b - p_{bc1})^{-t}$ in the lower conductivity stair and as $1/(R_1)(p_b - p_{bc1})^t$ in the upper conductivity stair. The general p_b dependence of the conductivity of the system will be given then by

$$\sigma(p_b) = \sum \sigma_n (p_b - p_{bcn})^t, \quad (11)$$

where σ_n is the appropriate local conductivity in the n th stair. Obviously the larger the $\sigma_n/\sigma_{(n+1)}$ ratio the sharper will be the conductivity transition around p_{bcn} (Balberg et al. 2013, see also Europhysics News 2014). The basic behavior conveyed by Fig. 4 will be shown in section “Universal and Non Universal Behaviors of the



Principles of the Theory of Continuum Percolation, Fig. 4 A schematic illustration of the staircase behavior of two stairs in the simple square lattice when the first nearest neighbors (small, R_1), and the second nearest neighbors (large, R_2), are involved in the electrical conductivity. Note

“Electrical Conductivity” to be important for the understanding of the behavior of many systems in the continuum.

Nonuniversal Behavior In the above considerations, we have assumed essentially a delta function distribution of the resistors’ values in the lattice. Our next concern will be the behavior of the conductivity for a general distribution function of the resistors values in the system. For simplicity we will only consider the nearest neighbor model for which, instead of a constant r_0 for all the resistors, we have the resistors value distribution $f(g)$ where the g are the local conductance values of the resistors. Obviously, in such a case we have to consider some average values of the resistances of the resistors involved. Let us assume now that the system has a bond occupation probability p_b and that the percolation threshold is p_{bc} , such that we consider the relevant, $p_{bc} < p_b < 1$ “conducting” interval. We have seen that in the lattice (Eq. (8)) the resistance of the system is determined by R_ξ . In the case of the distribution of the resistors values we can write $R_\xi = \langle r \rangle A_R L_1^\zeta$ instead of $R_\xi = r_0 L_1^\zeta$, where $\langle r \rangle$ is the average values of the resistances in the system (and thus in the backbone) and A_R is some

that in the low p_b region the resistance is determined by both types of resistors $\langle R \rangle_2$ while in the high p_b regime the resistance of the system will be determined practically only by the low resistance value R_1 . (From Balberg et al. (2013) and Europhysics News (2014))

($p_b - p_{bc}$ independent) constant parameter that accounts for the local and global geometry of the system. The issue of interest here is then the critical behavior of R_L when we have such a distribution of the individual resistance values. For addressing this issue let us denote the conductance of the individual resistor by g , so that the local value of the resistance is given by g^{-1} . Now suppose that the g values are taken from a distribution $f(g)$ that is confined to the range $g_1 \leq g \leq g_2$. Hence,

$$\langle r \rangle = \langle g^{-1} \rangle = g_1 \int_{g_1}^{g_2} g^{-1} f(g) dg. \quad (12)$$

We note here that this average is taken on $1/g$ (rather than on g), since it is the series connection of resistors that determines the resistance of the link, R_ξ . In principle, g_1 can be any value in the interval $0 < g_1 \leq g \leq g_2$ (a $g_1 = 0$ value corresponds to an unoccupied bond), and it is apparent that for a well-defined finite constant $g_1 > 0$, the critical behavior described by Eq. (9) with $\langle r \rangle$ replacing r_0 , will be the same as in Eq. (10). Correspondingly, the universal (lattice-like) critical behavior will be maintained. Now we note that if $f(g)$ decreases as $g \rightarrow 0$, the value of the average $\langle r \rangle$ as defined by Eq. (12), will be

finite, as above. On the other hand, if $f(g)$ is a constant or it is increasing toward $g = 0$ (i.e., $f(g)$ diverges at $g = 0$), the value of $\langle r \rangle$ will be ∞ . In other words, if there are “enough” $g \rightarrow 0$ conductors in the system, the average will be determined by them and one will get that $\mathbf{R}_L \rightarrow \infty$.

To consider however the behavior of $\mathbf{R}_L$ in more detail (i.e., the way in which $\langle r \rangle$ diverges) for a non-decreasing $f(g)$ distribution as $g \rightarrow 0$, we use the following procedure. We start listing the values of the local conductances in the system in a descending order. This is done since, assuming that the system is already connected it will be the group of the top value conductors that, while keeping the system connected, will determine its overall conductance. The other lower value conductances can be imagined to be connected only in parallel, to the network of these top value conductances. Noting that in our lattice system such a network is only possible for $p_b > p_{bc}$, we can consider a p_{bc} fraction (or subset) of the p_b bonds, as these will still maintain the global conductance. Now we note that this applies to any p_{bc} of the p_b local conductors. This is in particular so for the p_{bc} group of the “top” g values of the above list. Assuming then that there is no correlation between the location of the bond and its attached g value, we can use the fact that any randomly selected subset of p_{bc} conductors includes (by definition) a percolating cluster, and conclude that the above chosen p_c subset of the top value conductors constitute a percolation cluster. Of course, the largest conductance value in the system, g_2 , is also the largest possible g value in the so chosen subset. For convenience one can choose now the value of g_2 , by the relation $F(g_2) = 1$, where $F(g)$ is the indefinite integral of the function $f(g)$ that is given in Eq. (12). This is done without loss of generality since all other g values in the system can be normalized accordingly. On the other hand, the lowest g value of the conductors in the above p_{bc} subset of p_b has the corresponding normalized value g_c . Mathematically, this g_c value is given then by

$$p_b \left(\int_{g_c}^{g_2} f(g) dg \right) = p_{bc}. \quad (13)$$

This yields that (for $F(g_2) = 1$) $F(g_c) = (p_b - p_{bc})/p_b$, and thus that $g_c = F^{-1}[(p_b - p_{bc})/p_b]$, where F^{-1}

is the inverse function of F . We have then a very significant result that connects the conductors' values in the system with the proximity to the percolation threshold. In particular, it is the nature of the F^{-1} function that determines the “pace” at which $g_c \rightarrow 0$, as $p_b \rightarrow p_{bc}$. Having the result of Eq. (13) we can turn now to derive a quantitative determination of the critical behavior of $\mathbf{R}_L$ by evaluating the value of $\langle r \rangle$. The average resistance of the above defined subset, that we call here $\langle r_c \rangle$, is given by

$$\langle r_c \rangle = \int_{g_c}^{g_2} g^{-1} f(g) dg. \quad (14)$$

Following the above we recall that any other subset of p_c resistors will have an $\langle r \rangle$ which is larger than $\langle r_c \rangle$ (or equal to it), and thus $\langle r_c \rangle$ yields the lowest estimate of $\langle r \rangle$ that replaces $\mathbf{r}_0$ in Eq. (9). Considering the fact that we are concerned with $p_b \rightarrow p_{bc}$ and that $g_c \rightarrow 0$ there, the contribution of the very small g ($g < g_c$) values to the “measured” network resistance becomes negligible (Miller and Abrahams 1960). Hence, this $\langle r_c \rangle$ becomes a “more and more” accurate estimate in the $g_c \rightarrow 0$ limit, and consequently a reasonable replacement for $\mathbf{r}_0$. In what follows we demonstrate the consequences of the presence of such a divergent $f(g)$ function, in light of the seminal analysis of Kogut and Straley (1979). In particular, this is the superposition of the $(p_b - p_{bc})$ dependence of $\langle r_c \rangle$ on the universal critical behavior that was given in Eq. (10).

The Model of Kogut and Straley and Beyond As we have shown above, the crucial factor in the determination of the critical behavior of an average dynamical property is the variation of its extreme value as $p_b - p_{bc} \rightarrow 0$. Kogut and Straley (hereafter K&S) have proposed a particular distribution of the local conductances in a system that can yield the three basic physical behaviors (as reflected by their $p - p_c$ dependence) that can be obtained for such a dynamical property in a percolation system. Their normalized distribution function that turned out to be very useful for the description of the best known “real systems” (Balberg 1987a; Feng et al. 1987) yielded then analytic expressions for the diverging or non-

diverging $\langle \mathbf{r}_c \rangle$ values as $p \rightarrow p_c$. The distribution that they suggested was

$$f(g) = (1 - \alpha)g^{-\alpha} \quad (15)$$

which is normalized for $\alpha < 1$, in the range $0 < g < 1$. For this distribution one gets from Eqs. (13) and (15) that (for $g_2 = 1$)

$$g_c = [(p_b - p_{bc})/p_b]^{1/(1-\alpha)}, \quad (16)$$

and from Eqs. (14) and (15) that

$$\langle \mathbf{r}_c \rangle = [(1 - \alpha)/\alpha][g_c^{-\alpha} - 1]. \quad (17)$$

We see here the three possible behaviors as follows. If $\alpha = 0$, we have that $f(g) = 1$ and $\langle \mathbf{r}_c \rangle$ has a logarithmic divergence with $(p_b - p_{bc})/p_b$. Here we note that (in spite of the $\alpha = 0$) this case is different from the case of the same constant value for all the resistors in the sample. This is since the latter distribution function is actually $\delta(g - g_0)$, where g_0 is some particular (prechosen) value in the $0 < g < g_2$ interval that is not dependent on g_c (and thus is independent of $p_b - p_{bc}$). In particular we note that in contrast, the probability $f(g) = 1$ (i.e., the $\alpha = 0$ case) over the interval $g_c < g < 1$ means that each value in this interval participates in the conduction and this includes also the smallest g_c . This inclusion yields then the weak logarithmic divergence that was mentioned above. If $\alpha < 0$, $\langle \mathbf{r}_c \rangle$ is not diverging as $p_b \rightarrow p_{bc}$, and (as can be seen from Eq. (17)) it is the constant $(1 - \alpha)/(-\alpha)$. That is, the system behaves in the $g \rightarrow 0$ limit as if it is made of local resistors that are all having the latter average value.

The resistance dependence of most interest (see section “[Universal and Non Universal Behaviors of the Electrical Conductivity](#)”) is however the $0 < \alpha < 1$ case where, as seen in Eq. (17), when $p_b \rightarrow p_{bc}$ (i.e., when $g_c \rightarrow 0$),

$$\begin{aligned} \langle \mathbf{r}_c \rangle &\approx [(1 - \alpha)/\alpha]g_c^{-\alpha} \\ &\propto (p - p_c)^{-\alpha/(1-\alpha)}. \end{aligned} \quad (18)$$

Following that and recalling Eqs. (8), (9), and (10), one has that the resistance of the sample is approximated by $\mathbf{R}_L \propto \langle \mathbf{r}_c \rangle (p_b p_{bc})^{-t_{un}}$, where

t_{un} represents the effect of the global connectivity of the system. This yields that the critical exponent of the conductivity (see Eqs. (9) and (10)), will be given now by

$$t = t_{un} + \alpha/(1 - \alpha). \quad (19)$$

We see then that the model of K&S represents well all the three possible critical behaviors of the electrical conductivity. Mathematically this behavior exhibits the superposition of the critical behavior of the resistance (Eq. (18)) on the lattice stochastic behavior of the network, that is, the $p_b - p_{bc}$ dependence as given by Eqs. (8), (9), and (10).

The deviation of Eq. (19) from the universal behavior of the connectivity as given by Eq. (10) is known as the nonuniversal behavior. We note however that, historically, since such a non-universal behavior has been found in continuum systems, it has also been associated with the continuum nature of the studied systems. As will be seen below, the richness of nonuniversal behaviors in continuum systems seems to be the source of this confusion in the nomenclature. However, in this review, for the sake of a clear presentation, we use the term continuum to describe systems that are structurally different from lattices (see section “[Between Lattice and Continuum Percolation](#)”), and we use the term nonuniversal for all phenomena that yield critical exponents that differ from those of the classical ones (Stauffer and Aharony 1992) such as the one given by Eq. (10). This is in particular so for the electrical conductivity (and other dynamical properties (Balberg et al. 1988)) where $t \neq t_{un}$. In section “[Universal and Non Universal Behaviors of the Electrical Conductivity](#)” we will show that the mapping of the most conspicuous systems in the continuum onto the K&S distribution is possible and that it is associated with corresponding local geometrical parameters. We will also note the very important case where this mapping is not simple and other approaches must be taken for the determination of the $\mathbf{R}_L$ dependence on $p_b - p_{bc}$ as the percolation threshold is approached.

We have mentioned above the effective medium regime of the behavior on lattices (Kirkpatrick 1973; Sahimi 2003). The interest in that regime is primarily concerned with electrical properties, in particular with the electrical conductivity. The

corresponding EMA (mentioned in section “[The Critical Behavior of Percolation Clusters](#)”) yielded the asymptotic

$$\sigma(p_{be}) \propto (p_{be} - p_{bec})^v, \quad (20)$$

dependence with the a universal (here a dimension independent) exponent of $v \equiv 1$ and lattice dependent asymptotic threshold p_{bec} that as expected (apart from the square lattice case) is larger than p_{bc} . In passing we remark that the nonuniversality that we were concerned with above has to do with a dynamical property and thus the superposition of an $\alpha/(1-\alpha)$ like term applies also in the case of this effective medium regime (Sahimi 2003).

Experimental Confirmations and/or Explanations of Experimental Results

There were many computer-simulation studies that confirmed the nonuniversal behavior on lattices but as far as we know, unlike the many experimental confirmations that were found in continuum systems (see sections “[Between Lattice and Continuum Percolation](#)” and “[Percolation in the Continuum](#)”), no corresponding experiments were attempted in lattices:

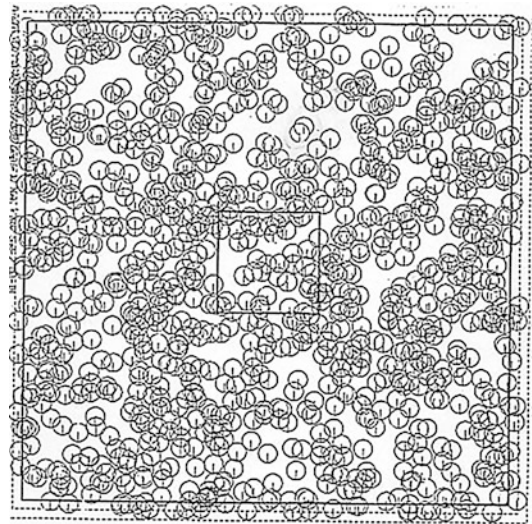
Between Lattice and Continuum Percolation

Major Issues in Continuum Percolation

Having the basic principal concepts of lattice percolation, we are now in a position to consider the major issues in continuum percolation. However, due to the limited scope of this review and the diversity of those issues we will focus here only on the ones that will represent those issues, that is, the structural and electrical properties. As we briefly reviewed above, lattices are systems that have sites (or bonds) with well-defined locations and they can be empty or occupied with a probability p_b or p_s . This yields percolation thresholds that depend on the particular lattice of interest. Also, the physical properties that are associated with the existence of the corresponding bonds in the system, are all characterized by the same single-valued physical parameters such as the

electrical resistance of the bonds. In continuum percolation, the system is composed of objects (or structures) that are randomly placed in space, that may be of various sizes and various shapes and that can also be interacting with each other. In particular, the physical parameters that characterize the bonds may vary from one bond to another in a manner that may or may not be determined solely by the local geometry and environment of the bond. The two most significant issues that are of concern in continuum percolation are then the connectivity of the system as reflected by the percolation threshold and the non-lattice like critical behavior of the geometrical and physical properties. To make this general discussion more specific let us consider an illustration of a well-known prototype of a two-dimensional continuum percolation system that consists of randomly distributed circles, as shown in Fig. 5.

The circles in this figure can be described as permeable, overlapping, interpenetrating, or of having a “soft core.” Such a system can represent

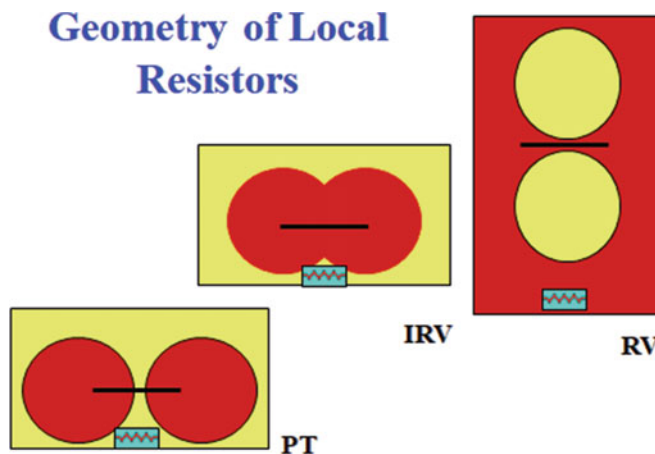


Principles of the Theory of Continuum Percolation, Fig. 5 A two-dimensional illustration of a continuum system. The circles are distributed randomly and two of them are considered connected if they partially overlap. There are finite clusters of connected (overlapping) circles as well as an “infinite” cluster of such connected circles. A small finite portion of the system is enclosed in the square shown at the center. (From Wagner and Balberg 1987)

a metal sheet in which holes have been drilled at random. In this case the electrical conduction, between opposite edges of the sample, is carried by the “background” (the sample without the holes) of the sheet and the bonds are associated with the gaps between two objects. We call this model of the system, the random void (RV), or the “Swiss Cheese” model (Feng et al. 1987). The system shown in Fig. 5 can be also considered as representing the mirror image of the RV system, that is, to represent pores (with a conducting liquid) in a porous medium (Hunt and Ewing 2009; Balberg et al. 1988; Balberg 1986), or a collection of isolated and fused metallic grains embedded in an insulating matrix such as in granular metals (Abeles 1976; Balberg et al. 1990; Fonseca and Balberg 1993). In those cases, the conducting parts are the pores or the grains, and their network provides the global conductivity of the system. The transport in those systems can be of a liquid or an electrical charge. Correspondingly, this view of the system is known as the inverted random void (IRV) model (Balberg et al. 1988; Sen et al. 1985). In the latter model the criterion for local connectivity (that is equivalent to the simple bond connection in lattice percolation) is rather simple;

two circles are connected if they partially overlap. The connectivity criterion in continuum systems is not always as simple. For example, let us consider a collection of randomly placed non touching metallic particles in which electrical current can pass between them, say, by electrical tunneling. In this case while the particles are not geometrically connected they are electrically connected. The fact that the latter property also involves a nontrivial distribution of the electrical conductances between all the particles in the system (Balberg 1987a; Johner et al. 2008) further demonstrates the complications that can arise in the continuum in comparison with the simple cases that are encountered in the classical lattice systems. We call here the model associated with the latter case the percolation tunneling (PT) model. In Fig. 6 we present an illustration of the three major types of connections that one encounters in continuum percolation and which have no counterparts in lattice percolation.

It is already the first examination of the systems shown in Fig. 6 that makes one appreciate the fundamental questions of continuum percolation. These are, how to define quantitatively the percolation threshold in such a system (there is no apparent meaning to p_s or p_b) and how does the



Principles of the Theory of Continuum Percolation, Fig. 6 The three major configurations of “real” systems in the continuum. The red color represents the conducting phase and the yellow color represents the insulating phase in the systems. The bars and the resistors represent the “necks” and the corresponding dominant local resistors in the system. The three configurations represent, from

right to left, the random void (RV), the inverted random void (IRV), and the percolation tunneling (PT) models. In the RV, one is concerned with the gap between the systems’ nonconducting objects; in the IRV, one is concerned with overlap between the (permeable) conducting objects; and in the PT, one is concerned with the separation between two conducting objects. (From Balberg 2009a)

local degree of the objects interaction (say, overlap) determine the local and global geometrical and dynamical properties of the system. It is obvious then that new concepts and new extension of the well-established lattice theory are needed in order to describe quantitatively the conspicuous percolation phenomena that are encountered in the continuum. These primary issues will be discussed in section “[Percolation in the Continuum](#)” of this review, leaving out, for brevity and simplicity, the discussions on numerous natural and artificial systems and their properties for which the consequences of the above issues are of great significance.

The Historical Bridges Between Lattice and Continuum Percolation

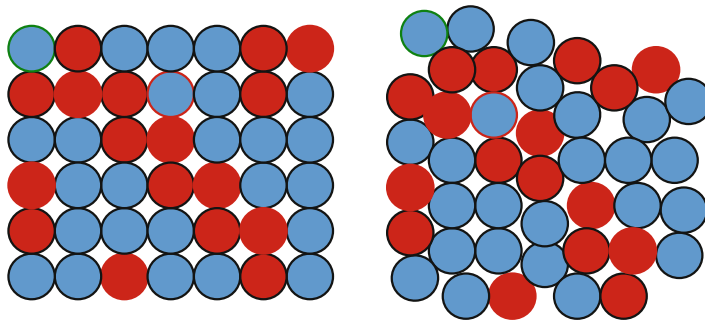
The first attempt to characterize the percolation threshold in the continuum, which is usually credited as the beginning of the field of continuum percolation was the 1970 (Scher and Zallen 1970) work of Scher and Zallen (S&Z). They have based their argument on the “behavior” of the onset of global connectivity in systems that, while including objects (rather than sites or lattice segments), are based on lattices, such as in the left panel of Fig. 7.

As in the lattice models described in section “[The Percolation Thresholds](#)” the red (say, the conducting) spheres occupy lattice sites, with a probability p_s . The blue (insulating) spheres correspond to empty sites in the lattice. The local connectivity criterion here is simply the exact

touching of nearest (red) neighbor spheres. Hence, if the diameter of the hard-core spheres is equal to the lattice spacing the connectivity of the network stays the same as in the corresponding lattice. We can consider then the volume fraction of the conducting (red) phase which is simply given by $x = p_s f$, where f is the filling factor of the system (the maximum fraction of the volume in a given unit volume in the lattice that can be filled by hard spheres of equal size). Correspondingly, one can define the percolation threshold by the total occupied volume fraction of the conducting spheres, that is, by $x_c = p_{sc} f$ that yields a cluster of connected spheres that reside exactly on the cluster of the connected sites in the corresponding lattice with the same p_s . It is obvious then that $x - x_c \propto p_s - p_{sc}$ and that the critical behavior of a given property Ξ in this case will be determined by

$$\Xi \propto (p_s - p_{sc})^\chi \propto (x - x_c)^\chi \quad (21)$$

where χ is a corresponding-lattice critical exponent. S&Z noticed that x_c , unlike p_{sc} (or p_{bc}), is nearly a dimensional invariant, yielding values very close to 45 (area %) for all 2D lattices and very close to 16 (vol.%) for all 3D lattices. This brought them to propose that, if one “shakes” the lattice-like system shown in the left panel of Fig. 7 to yield a disordered system of touching spheres, its macroscopic topology (see Fig. 3) will not be significantly modified. Thus, following the above



Principles of the Theory of Continuum Percolation, Fig. 7 The left panel is an illustration of a small portion of a square lattice that is comprised of “conducting” (red) and “insulating” (blue) circles. The local connectivity is defined here by the “single point” contact between two

red circles and the global connectivity is determined by the spanning cluster of touching red circles. The right panel represents the same stochastic (same concentrations of the spheres) system but a different topological (“disordered”) one, on the local scale. (From Balberg 2009a)

close invariance, they suggested that x and x_c will be as good parameters as p_s and p_{sc} are for lattices, for the characterization of the disordered arrangement of spheres. The “shaked” system that is illustrated in the right panel of Fig. 7 can be also envisioned as a result of randomly “dropping” red and blue spheres “gravitationally” into a container so that the “gravitation” secures the (single point) contacts between adjacent spheres (Powell 1979). Following the above-concluded topology, it was of no surprise then that the latter approach confirmed the ideas and the results of S&Z and thus provided the first indication that the properties in the continuum can be mapped onto their well-understood counterparts in lattice percolation. We note of course that the above systems are by no means general, or a prototype, of a continuum system (Balberg and Binenbaum 1987a). Rather, it represents an example of simple mapping of a continuum problem onto a lattice problem. While the use of the fractional volume as a percolation parameter, which is equivalent in the abovementioned way to the p_s in lattices, was an important step in launching a theory for continuum percolation, their x_c values were misused later, by many. In fact, this is still ignored in many works, and some authors use those values for the characterization of continuum systems that are very different from the ones for which the above very particular values (that are characterized by a secured single-point contacts) were calculated (Balberg and Binenbaum 1987a). For example, consider a system of red spheres that are embedded randomly in a continuous insulating matrix. It can be easily appreciated that $x_c = 16$ vol. % in such a system of hard spheres yields a very sparse “none-percolating” composite and that the metallic (touching grain) connected network will be set at a much higher vol. % (of the order of 50 vol. % in the granular metals (Abeles 1976) as indicated by Fonseca and Balberg (1993)). Moreover, in practice there is no random system in which the “contact” or the “bond” between nonpermeable elements is “automatically” provided (if at all, it is approached only at the very high close packing limit of $x > 64$ vol. % (Heyes and Melrose 1998; Ziman 1979; Zallen 1983)). Hence, there is no resemblance between the abundant common composite (where the conducting particles are embedded in a

continuous insulating matrix) and the models of S&Z and Powell (1979), and thus the value of $x_c = 16$ vol. % is by no means a general approximate-invariant. This problem was discussed in more detail by Balberg and Binenbaum in 1987 (Balberg and Binenbaum 1987a). The more rigorous approach to the percolation thresholds in continuum systems that was provided by Shante and Kirkpatrick (S&K) (Shante and Kirkpatrick 1971) in 1971 and extended by Balberg et al. in 1984 (Balberg et al. 1984a) and 2012 (Balberg 2012) will be described in the next section.

Percolation in the Continuum

In this section we describe the fundamental strides in the theory of continuum percolation and some of the recent development in that theory.

The Percolation Threshold in the Continuum

In 1971 (Shante and Kirkpatrick 1971) Shante and Kirkpatrick (S&K) approached the percolation problem from the opposite end to the one of S&Z, that is, considering permeable objects as in the case shown in Fig. 5. Similarly to S&Z, it was obvious to S&K that the most promising approach for the evaluation of continuum systems is to try to consider them as asymptotic cases of lattice systems, for which the theory was quite developed in the 1970s. They took what may be considered the most important single step in correlating lattice percolation and continuum percolation. This is by proving that the topology of the two can be mapped onto each other. Their approach took into account an earlier empirical observation of Dalton, Domb, and Sykes in 1964 (Dalton et al. 1964) that in lattices, where z (the coordination number, i.e., the number of nearest neighbor sites in various lattices (Zallen 1983)) approaches infinity, the value of the product $B_c = zp_{sc}$ extrapolates to 4.5 in 2D and to 2.8 in 3D. Hence, the quantity zp_{sc} can be very useful in cases where $z \rightarrow \infty$ as is the case of a system of permeable objects where one can “implant” them anywhere in space with no limitation. In particular, for permeable spheres, as in Fig. 5, the density of possible centers of spheres that overlap a given sphere is unlimited. In passing

we remark that B_c here (Zallen 1983) is different than the B_{bc} that we mentioned above for the bond problem since, while both are dimensional invariants they apply for different limits of z (Balberg and Binenbaum 1987b). We further remark here that while $p_b = p_s^2$, this does not yield that $p_{bc} = p_{sc}^2$ simply because the local topology of the site and the bonds are very different for the same lattice. For example, in the square lattice the site has four nearest neighbors while the bond has six nearest neighbors. It is not surprising then that p_{sc} is always larger than p_{bc} . Hence, as considered below, there is a difference between $B_{bc} = zp_{bc}$ and $B_c = zp_{sc}$ and in particular it is always that $B_c > B_{bc}$ (Balberg and Binenbaum 1987b).

The Concept of the Excluded Volume and Its Consequences

Following the above observation, S&K conjectured that the topology of the $z \rightarrow \infty$ lattice and the continuum systems of permeable spheres is the same at the onset of percolation, that is, the number of occupied sites around a given site then, and the number of overlapping spheres for a given sphere will be the same. In other words the topology of these two systems is expected to be the same at the onset of global connectivity. To test this idea, S&K considered the fact that the probability of randomly choosing a geometrical point that will be out of a given permeable sphere of a volume v , in a unit size system, is $(1-v)$. The probability that this point will be out of all the ρ_c spheres in the system at the percolation threshold is $(1-v)^{\rho_c}$. In a large system that is statistically sufficient (i.e., $v \ll 1$ but $\rho_c \rightarrow \infty$) we can write the latter quantity as $e^{-v\rho_c}$. On the other hand, the probability of a point to be in any of the spheres (at the onset of percolation) is simply ϕ_c , the fractional volume that is covered by the ρ_c spheres. Hence, $\phi_c = 1 - e^{-v\rho_c}$. For a permeable sphere of radius a , in order not to overlap a given sphere, its center has to be at least at a distance of $2a$ from the center of the given sphere. Correspondingly, the volume in which the center of the second sphere is not “allowed” to be (if no overlap is permitted) is not v but, rather, $8v$, or for hyperspheres in a D -dimensional system it is $v2^D$. This volume is known as the excluded volume of spheres (Shklovskii and Efros 1984). On the other

hand, the average number of centers of spheres that overlap a given sphere, at the onset of percolation, is simply $v(\rho_c)2^D$. We have then that the latter quantity is just the *critical number of connections to a given sphere* (or centers, or occupied sites in the lattice), B_c . Applying now the above continuum percolation conjecture of S&K, that is, that $B_c = zp_{sc}(z \rightarrow \infty) = v(\rho_c)2^D$, one finds that for a system of hyperspheres of dimension D

$$\phi_{Dc} = 1 - \exp(-B_c/2^D). \quad (22)$$

Using then the abovementioned 4.5 and 2.8 “lattice” values of B_c for $D = 2$ and $D = 3$, with the prediction of Eq. (22), S&K found an excellent agreement with the Monte Carlo simulations, finding of $\phi_{2c} = 68$ area % and $\phi_{3c} = 29$ vol.%. In fact, the B_c values were confirmed directly for permeable spheres later (in 1987 (Balberg and Binenbaum 1987b)) by Balberg and Binenbaum. In passing, we note that following the above argument for any system of parallel aligned “regular objects” (such as boxes or cylinders) the relation $B_c = (\rho_c)V_{ex}$ where V_{ex} is the corresponding excluded volume is expected to be obeyed (Balberg et al. 1984b; Skal and Shklovskii 1974; Xu et al. 2016).

In 1984 Balberg et al. (1984a) realized that the ideas of S&K can be generalized to nonspherical objects, and even to objects that have no “volumes” of their own. Such as in the case of two-dimensional “width-less sticks” (Balberg and Binenbaum 1983; Balberg et al. 1991), where the local connectivity criterion is the intersection of two of them, and the onset of percolation does not require any area of the sticks. This is in contrast with the systems mentioned so far. The way this generalization was conducted (Balberg 1986) followed the procedure of S&K with the topological expectation that for any system (regardless of the particular properties of its objects) B_c is the most meaningful general topological parameter, and as such, it is expected to be a finite invariant. Following the B_c values in lattices of various dimensions (Zallen 1983), their values are intuitively expected to be between 1 and 5 (Wagner et al. 2006). The rigorous derivation of the abovementioned B_c will be discussed below. Naturally, the simple relation we had above for spheres can be generalized now to all dimensions and all

types of permeable objects of a finite volume. This is done by noting that one can write ϕ_c by using, instead of $v(\rho_c)$, as above, the relation, $v(\rho_c)V_{ex}/V_{ex} = vB_c/V_{ex}$ for an object of hyper volume v and a hyper excluded volume, V_{ex} , thus yielding that

$$\phi_c = 1 - \exp - (B_c v / V_{ex}). \quad (23)$$

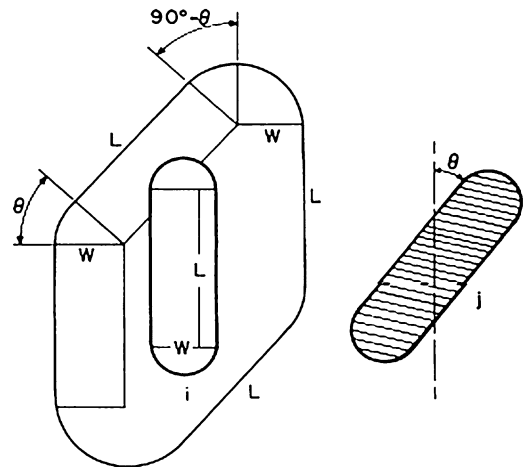
Following this relation, Balberg (1986) has noted in 1986 that Eq. (23) has far-reaching consequences, since it states that one can have a connected system with very minute content of the “percolating” or “conducting” phase ($v(\rho_c) = vN_c$ or ϕ_c). This follows from the fact, seen in Eq. (23), that ϕ_c can be as small as desired if v/V_{ex} is as small as required. Indeed, this result enabled to explain the $\phi_c \rightarrow 0$ values in porous systems (Balberg 1986), such as in sedimentary rocks (Archie 1942; Sen et al. 1981) and geological cracks (Shakland and Waff 1974), as well as in many composites (Sahimi 2003), including cellular composites (Vionnet-Menot et al. 2005; Pike 1978) where the conducting phase is well described by lines or planes (Robinson 1983). Moreover, the fact that for lattices we have always finite p_{sc} (or p_{bc}) values that are larger than 0.3 for 2D and larger than 0.1 for 3D made this result of ϕ_c values to be as small as desired, quite surprising. Moreover, this result demonstrated that the mapping of the continuum onto lattices is not as simple as might have been conjectured from the pioneering works of S&Z and S&K (who were concerned only with systems of spheres).

The above generalization of the application of the concept of the excluded volume is also very useful for systems with distributions of object sizes, shapes, and orientations. For those systems, when a proper determination of the average excluded volume of the system, $\langle V_{ex} \rangle$, is carried out (Balberg et al. 1984a; Drory et al. 1991), the above $B_c = (\rho_c)V_{ex}$ relation for permeable spheres can be generalized to

$$B_c = N_c \langle V_{ex} \rangle, \quad (24)$$

where N_c is the concentration of the objects at the onset of percolation. This result is very significant and important from the point of view of applications, since if B_c is nearly an invariant (as to be expected in view of the above) its value changes

only in a very limited range (see however below the paragraph on the “origin of the different B_c values in systems of different objects”). Correspondingly, by assuming a constant B_c , trends in the behavior of percolation thresholds N_c , as a function of the object’s parameters, can be readily derived (Balberg 1986; Charlaix et al. 1984; Laria and Vericat 1989; Saar and Manga 2002). Moreover, one can predict the actual vol.% of the conducting phase (ϕ_c or $N_c v$) by just knowing the values of B_c and $\langle V_{ex} \rangle$ that can be well approximated by corresponding models. It turned out then that the application of the concepts exhibited by Eqs. (23) and (24), beyond the very simple solution of $V_{ex} = 2^D v$ of S&K for spheres and by Pike and Seager (1974), and Skal and Shklovskii (1974) for parallel convex shaped objects in 1974, has enabled the application of the above considerations to very many continuum systems. This was done in particular by the use and/or modification of the most celebrated model of nontrivial systems, that is, that of the three-dimensional continuum system of capped cylinders (Balberg et al. 1984a). The capped cylinder of length L and diameter W and its excluded volume with respect to a given direction in space are illustrated in Fig. 8.



Principles of the Theory of Continuum Percolation, Fig. 8 The volume of a capped cylinder (dashed) and the excluded volume of two such cylinders. The latter is for two cylinders (i and j) when the angle between their axes is θ . (From Balberg et al. 1984a)

These capped cylinders span objects from spheres to cylinders with a single “close to an invariant” value of B_c . The basis of this model has been applied later by Berham and Sastry in 2007 (Berham and Sastry 2007) even to rather non-regular “wavy” shaped objects.

The system of capped cylinders became by now the prototype of continuum percolation systems of “nontrivial” (nonspherical) permeable (Balberg et al. 1984b) and nonpermeable (Balberg and Binenbaum 1987b) objects. The volume of the permeable capped cylinder of length L and radius $r = W/2$ is simply $v = \pi^2 L + (4\pi/3)(r)^3$, but its average excluded volume (over the possible inter-cylinders orientations) that is shown in Fig. 8 is given by (Balberg et al. 1984a)

$$\langle V_{ex} \rangle = (32\pi/3)r^3 + 8Lr^2 + 4L^2r \langle \sin(\theta) \rangle \quad (25)$$

where θ is the angle between two (possible) intersecting cylinders, and the average is over the particular distribution of the θ values (Balberg et al. 1984a; Neda et al. 1999). The “nontrivial” aspect is manifested by the fact that $\langle V_{ex} \rangle$ is not proportional to v , and that in the large aspect ratio case (i.e., $L \gg r$) one has that $v/\langle V_{ex} \rangle \propto r/L$, while for the small aspect ratio case we recover the abovementioned trivial $v/V_{ex} = 1/8$ result for spheres. The simulation confirmation of the relation suggested by Eq. (25) for the system of 3D capped cylinders has well exhibited the inverse dependence of the percolation threshold on r exhibiting the transition from the linear to the cubic dependence with the increase of r (Balberg et al. 1984b). Similar confirmations have been given for various distributions of $\langle \sin\theta \rangle$ (Balberg et al. 1984a; Neda et al. 1999).

The capped cylinders system that was described here can be shown to represent very many natural and artificial systems where the objects are slender (Charlaix et al. 1987) or have a negligible volume (Robinson 1983). We note also that another system that is very helpful for the description of various systems is that of disks with a radius a and a thickness t . These disks have a volume $v = \pi a^2 t$, while their excluded volume, in the isotropic orientation case, is given by $V_{ex} = \pi^2 a^3$ (Charlaix et al.

1984). It is apparent that in the thin disk limit ($t \ll a$), we get that $v/V_{ex} \propto t/a$, explaining the very small ϕ_c values observed in geological formations (Balberg 1986) and in various cellular composites (Chitame et al. 2003). In passing, we note that the low dimensionality of the conducting phase inclusions in these systems explains the correlation between low percolation thresholds and the pseudononuniversal critical conductivity that will be described in section “Further Extensions for Various Off-Universal Conductivity Exponents in Continuum Systems.”

Following the above, let us consider now the basic physics of the variations of B_c as one goes from systems that consist of permeable (soft-core) spheres to quasi-permeable spheres with a hard-core of radius b and a wrapping soft-shell with a thickness of $a-b$ (Balberg and Binenbaum 1987b). We mentioned already that the value of B_c is 2.8 in the 3D soft-core limit. We also know then, as found directly (Balberg and Binenbaum 1987a), that the value of B_c decreases with the increase of b , toward the bond, B_{bc} -like, value of 1.5 (Ziman 1979; Zallen and Scher 1971). What we have available empirically then are those two limits, the fact that what influences the behavior are volume quantities, and the above expectation that B_c will decrease between the two limits as $b/a \rightarrow 1$. Hence, we can simply expect empirically that

$$B_c = 1.5 + 1.3 \left[1 - (b/a)^3 \right]. \quad (26)$$

Considering the abovementioned topological meaning of B_c we recall that for lattices we had that in the $z \rightarrow \infty$ limit, $B_c = 2.8$, and we note that for the other, $z \rightarrow 1$, limit we can apply the conjecture of Ziman (1979) that $z p_{bc}$ is an invariant in lattices (such that $z p_{bc} = 1.5$ in 3D). Now, the smallest z (existing or imaginary) that is needed for percolation in 3D lattices is 1.5. In this case, we expect then that the approximation

$$B_c = 1.5 + 1.3[1 - (1.5/z)] \quad (27)$$

will be reasonable for lattices. If the connecting topology in the continuum and in lattices is the same, B_c should scale equally well for $(b/a)^3$ and

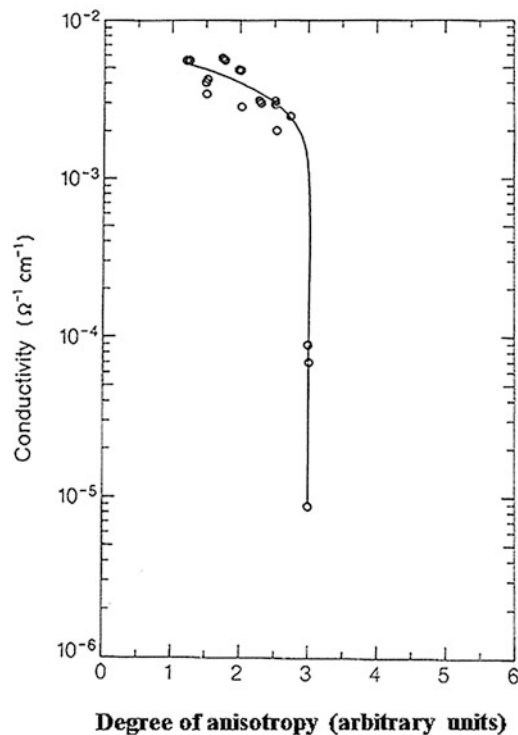
$1.5/z$. Indeed, Monte Carlo simulations on a series of systems that represent the “soft core” to the “hard core” transition (Balberg and Binenbaum 1987b) have confirmed this mapping of the continuum system onto the lattice system. This establishes that, indeed, the underlying connectivity is the same in lattices and in continuum systems of partially permeable spheres (i.e., beyond the S&K soft-core limit). We noted already that from the practical point of view, one can generally predict the percolation threshold B_c once one knows the value of B_c (or an approximate value of it) and the value of V_{ex} . In the present case of spheres we have the value of B_c (Eq. (26)) and $V_{ex} = (32\pi/3)(a^3 - b^3)$. Hence, as the hard-core limit is approached (and B_c gets the value of 1.5) we expect (see Eq. (24)) that for a system of a unit volume, N_c will diverge as the close packing limit is approached. These ideas were also well exhibited by Monte Carlo results for a system of spheres (Balberg and Binenbaum 1987b). It was also shown that the dependence of B_c on $(1.5/z)$ for three-dimensional lattice systems does indeed follow Eq. (27). This phenomenological behavior of the decrease of the B_c value represents then also a site percolation to a bond percolation transition as the thickness of the soft-shell decreases, where we recall that it is the permeability of the objects that enables an unlimited z value. We note here that the above does not tell us why the value of B_c itself decreases in the $b/a \rightarrow 1$ and $z \rightarrow 1.5$ limits but considering the B_c values it is clear that these limits are associated with the larger number of bond neighbors than site neighbors in lattices. As will be shown further below, if the system consists of hard-core particles that have extreme aspect ratios, the corresponding excluded volume argument of the soft-core case (as in Eq. (25)) is also applicable. In particular, the anisotropic behavior is given then by the same $\langle \sin\theta \rangle$ dependence that was mentioned here for the soft-core case.

Experimental Confirmations and/or Explanation of Experimental Results Many computer simulations have studied the dependence of the percolation threshold on the aspect ratio of the objects and the ensemble’s degree of anisotropy,

$\langle \sin\theta \rangle$, in the system. On the other hand, there were only very few experimental works that confirmed the behavior predicted by Eq. (25). Following the similar behavior of systems where the particles have a high aspect ratio, whether permeable or not (see the last paragraph in this subsection), we show in Fig. 9 a corresponding experimental confirmation that shows that at a certain degree of anisotropy (that is related to $\langle \sin\theta \rangle$) the composite ceases to conduct. In other words, by increasing the anisotropy the system reaches its percolation threshold.

Effect of Particle Interactions on the Percolation Threshold

A somewhat different view of the hard-core/soft-shell problem enables to examine continuum percolation properties that can be considered even



Principles of the Theory of Continuum Percolation, Fig. 9 The experimentally found dependence of a composite’s conductivity on the global anisotropy of the system. The 0 anisotropy represents a system where the elongated carbon black particles in the composite are distributed isotopically while 6 represents the case where they are practically parallel to each other. (From Balberg 1987b)

more remote from those of lattice systems. A conspicuous case of such a property is the effect of objects interaction due to an interaction (or the potential) associated with the objects (Chiew and Glandt 1983; Netemeyer and Glandt 1986). To introduce this scenario, we can consider the above hard-core/soft-shell spheres as being composed of a region of infinite repulsive interaction at distances r (from its center) smaller than $2b$, and a shell of zero potential for $r > 2b$. We may further look at the problem as a one in which the density of the objects is not uniform around an object (here, e.g., $\rho = 0$ for $r < 2b$ and $\rho = \rho_1 (> 0)$, for $r > 2b$). If we use then the corresponding radial distribution function $g_R(r)$ of the particles (or objects' centers), the average number of bonds per site will be given by $B = \langle \rho \rangle \int_0^{2a} g_R(r) d^3r$. Here $\langle \rho \rangle$ is the average density of objects in the whole system and a is the radius of the soft-shell (that determines the local connectivity of the system). If we have a more complicated potential (i.e., when $g_R(r)$ has values different from 0 or 1 as above), B , and thus B_c , will depend on the parameters of this distribution, such as on the interaction potential that determines the $\rho(r)$ dependence (Alon et al. 1991). A case that was considered in detail and is relevant, for example, to micro emulsions (Grest et al. 1986), is that of an attractive potential shell that “wraps” the hard core ($b \leq r \leq (1 + \lambda)b$) and has a constant, nonzero value, in the interval of λb . In that case, it has been shown first by Grest et al. (1986) and Bug et al. (1985a) (and later by Drory et al. (1994, 1995)) that interactions can raise or lower the percolation thresholds. This is that the value of the global ρ_c value is determined by the details of the magnitude of the potential and the ratios between b , λ , and a . Physically, this non-monotonic behavior is not too surprising. This is since the attractive potential will cause the increase of the density of objects in the attractive potential region, but for a globally given ρ , it will cause a reduction of the density outside this region. The two effects will be manifested by an increased probability for the formation of connected clusters, on the one hand, but by the reduction of the connectivity between different clusters, on the other hand. The interesting observations are then the

nontrivial results of the interplay between these two effects as determined by the potential parameters, that is, by the dependence of the values of B_c and ρ_c on them. From the point of view of continuum percolation theory, the important conclusion is that even in this complicated interaction case we can characterize the system by its B_c value and correlate it with system parameters. This enables to generalize the percolation approach to systems where the mapping onto lattice models is, conceptually and/or computationally, not obvious. On the other hand, it is apparent that corresponding derivations can account for general connectivity problems where other “bonding strength” parameters are not uniform in space or in the network.

The Origin of the Different B_c Values in Systems of Different Objects

So far, we have taken B_c to be an empirical parameter, as are the p_{sc} and p_{bc} quantities in lattice percolation. The application of the relation given by Eq. (24) has been proven to be extremely useful for the determination of trends in the variation of measurable percolation thresholds (i.e., ρ_c or N_c) when a constant (system independent) B_c value was assumed (Wagner et al. 2006; Drory et al. 1991). However, the various values of B_c , while being confined to the 1–5 range (see above) are not the same for systems of objects of different shapes. These differences are important to understand since, as we discussed above, this is the only parameter that accounts for the global topological connectivity of percolation systems in the continuum. We note in passing that while the B_c values can be derived rigorously (see below), their relation to the particular objects in the system under consideration is not a priori transparent from the corresponding derivations. At this point, we concentrate then on the reasons for the different B_c values for different “types” of objects. For example, B_c is 2.8 for permeable spheres but it is only 2.6 for parallel permeable cubes. While this difference seems minute (in comparison with the larger differences to be mentioned below), it is a convenient case for the illustration of the concept of “pointedness” that enables to explain the differences in the observed B_c values. The reason for the abovementioned variations in the B_c values

has hardly been considered prior to the work of Alon et al. in 1991 (Alon et al. 1991) that yielded an insight into the apparent “different topology” associated with different objects. They derived this understanding using a heuristic or “semi-rigorous” argument, which will be illustrated here by the different B_c values for spheres and cubes (Alon et al. 1990), as well as by the variation of B_c in the soft-core to hard-core transition (Balberg and Binenbaum 1987b). Again, this effect on global connectivity has no analog in lattice percolation.

To appreciate the corresponding argument let us consider a system of permeable spheres of radius r_1 and a system of parallel permeable cubes with an edge a_1 . Choosing their size such that they have the same excluded volume $\langle V_{ex} \rangle$ (in this case, also the same volume), we note that in both cases we set $\langle V_{ex} \rangle = (4\pi/3)(2r_1)^3 = (2a_1)^3$. Now let us consider the maximum distance between the centers of two spheres that can overlap. This distance is $2r_1$, and thus the possible distances, ℓ_1 , between the centers of two partially overlapping spheres is in the range $0 \leq \ell_1 \leq 2r_1$. In contrast, for the three-dimensional cubes that are also connected by a partial overlap (and have the same $\langle V_{ex} \rangle$), the corresponding range is $0 \leq \ell_1 \leq \sqrt{3}a_1$, that is, $0 \leq \ell_1 \leq 2.7r_1$. Hence, since the density of the centers of the objects is uniform in both cases two partially overlapping cubes can, on the average, “span” a larger distance than that of partially overlapping spheres. Correspondingly, in order to span an “infinite” cluster, there will be a need for a smaller number of cubes than spheres, that is, the value of ρ_c will be smaller in the case of cubes compared with that of the case of spheres. Since we have chosen V_{ex} to be the same in the above two systems, the corresponding value of ρ_c and thus the value of $B_c (= \rho_c V_{ex})$ will be lower in the case of the cubes. Of course, the exact ratio between the B_c values of the two systems cannot be derived from the qualitative simple illustration given here, but a more refined argument has been shown to heuristically yield such ratios exactly (Alon et al. 1991).

Since the apparent difference between the cube and the sphere is that the former has corners (“points”), one can say that the “pointedness” (that was defined accurately by Alon et al. (1991)) brings

about the lower value of B_c . We can correspondingly conclude that since the average “covered” ℓ_1 “per excluded volume” will be larger, the higher the aspect ratio of elongated objects, such as boxes that are isotopically distributed in space (Drory et al. 1991). We can further expect that for elongated boxes, of the same $\langle V_{ex} \rangle$, the value of ρ_c will decrease with this ratio. For these objects, as mentioned above, the corresponding trend of the decrease of B_c with the aspect ratio was confirmed both rigorously and computationally (Wagner et al. 2006; Drory et al. 1991), to decrease from about 2.7 to 1.2 for aspect ratios between 1 and 500. The latter trend was confirmed also for other types of permeable elongated objects (Saar and Manga 2002; Berham and Sastry 2007).

A similar argument can apply to the above-mentioned B_c difference between the behavior of spheres with a hard core of radius b and a soft-shell with a wrapping thickness of $a_1 - b$. The “local span” of the two objects’ in the $b = 0$ case is in the $0 \leq \ell_1 \leq 2a_1$ range, while for the hard-core sphere with a soft-shell it is $2b \leq \ell_1 \leq 2a_1$, so that the average ℓ_1 value is larger in the latter case. Correspondingly, the “span” of larger hard-core spheres will be larger, or the value of ρ_c will be smaller in the hard-core/soft-shell case, suggesting the decrease of B_c from 2.8 to 1.5, as we argued phenomenologically in Eq. (26). The above result is of great conceptual importance, since it shows that while the phenomenological theory of the excluded volume theory was developed for permeable objects, *all consequences regarding the trends in the values of the percolation thresholds (such as the effect of the aspect ratio) apply also upon the approach to the hard-core limit*. In fact, from the above arguments concerning the aspect ratio and the soft-core to hard-core transition, we conclude that the two effects can be compounded. *This is also important from the practical point of view*, since one can be guided, for example, for “real” composites that are composed of hard-core objects (Balberg 2012; Balberg and Bozowski 1982). A case in point is the decrease of the percolation threshold in carbon-black-polymer composites as the conducting particles (or, as better known, “higher

structure” particles) (Berham and Sastry 2007; Rubin et al. 1999; Ahmad et al. 2006) become elongated. We remark here that, in a way, the different percolation thresholds due to the point-ness is analogous to the different percolation thresholds of lattices as they can have many values in the same dimension. As generally for continuum percolation, this phenomenon is, however, much richer since there are many more shapes (and their soft and hard cores) than the numbers of nearest neighbors in lattices at a given dimension.

Rigorous Quantitative Determination of the Percolation Threshold

Thus far, we got the values of the thresholds in the continuum by either applying lattice quasi-invariants (notably p_{scz} for $z \rightarrow \infty$), heuristic arguments (Alon et al. 1991), or computer simulations (Balberg and Binenbaum 1987b; Balberg et al. 1984b). Noting that a “complete” theory with a firm basis requires a rigorous derivation of the fundamental quantities from first principles, it is always a challenge to achieve such a derivation beyond the experimental and computational observations and their trends. This challenge was recognized also for the problem at hand, that is, the rigorous finding of the “fundamental-topological” percolation threshold B_c (e.g., $B_c = 4.5$ for circles and $B_c = 2.8$ for spheres), which we encountered in the previous sections. The above challenge was met at first by the application of graph theory for the analogous lattice-bond percolation problem. The corresponding attempt, which involved a lengthy cluster enumeration and high-order overlap-integrals, has not been followed, probably because of the latter reasons. The breakthrough in trying to provide a rigorous route, which is physically more transparent, can be attributed then to the work of Coniglio, DeAngelis, and Forlani in 1977 (Coniglio et al. 1977). For the above purpose, they applied the formalism of the connectedness functions that is well known in the theory of liquids (Hansen and McDonald 1986). For the sake of brevity, we will describe here their approach only by the following simple “intuitive” arguments.

If we define a local (direct) connectedness criterion (e.g., overlap between permeable spheres) and a global connectedness (i.e., being on the same cluster), we can derive a direct connectedness function $C(\mathbf{x}, \mathbf{y})$. For this function, if $\mathbf{r}$ is the vector $\mathbf{x}-\mathbf{y}$ connecting “directly” the two objects at $\mathbf{x}$ and at $\mathbf{y}$, $\rho(\mathbf{r})C(\mathbf{r})d^3r$ is the probability that for a given particle at $\mathbf{r} = \mathbf{0}$, there will be a particle, in the volume d^3r around $\mathbf{r}$, that is locally connected to the particle at $\mathbf{r} = \mathbf{0}$. Here, $\rho(\mathbf{r})$ is the particles’ (or objects’) density in the system. The quantity $C(\mathbf{x}, \mathbf{y})$ accounts, in addition to the direct connection, for all possible additional “indirect” connections between the two “directly connected” particles, and thus it can be presented by corresponding “closed diagrams” (Drory et al. 1997). Similarly, one can define a “total” pair connectedness function $g(\mathbf{z}, \mathbf{y})$ between two objects (say, at $\mathbf{z}$ and at $\mathbf{y}$) which involves all the connecting (direct and indirect) routes between them. The function $g(\mathbf{r})$ (where $\mathbf{r} = \mathbf{y}-\mathbf{z}$) can be defined then by the probability, $\rho(\mathbf{r})g(\mathbf{r})d^3r$, of finding a particle in the volume element d^3r around $\mathbf{r}$, which is connected (i.e., belonging to the same cluster) to the particle that is assumed to exist at $\mathbf{r} = \mathbf{0}$. Since $g(\mathbf{x}, \mathbf{y})$ is composed of “direct” connectivity steps such as $C(\mathbf{x}, \mathbf{z})$ and $C(\mathbf{z}, \mathbf{y})$, the “total” $g(\mathbf{x}, \mathbf{y})$ function can be expressed by the corresponding (Ornstein-Zernike) “chain” rule

$$g(\mathbf{x}, \mathbf{y}) = C(\mathbf{x}, \mathbf{y}) + \int \rho(\mathbf{z})C(\mathbf{x}, \mathbf{z})g(\mathbf{z}, \mathbf{y})d^3z, \quad (28)$$

where $\rho(\mathbf{z})$ is the density of particles (or centers of objects) in a volume of d^3z around $\mathbf{z}$. For simplicity we will assume in the following that $\rho(\mathbf{z}) = \rho$, where ρ is a constant-uniform density in our problem. The crucial step that connects relation (28) with the present continuum percolation problem (i.e., with the average cluster size) is the consideration of its Fourier transform. For a “wave vector” $\mathbf{k}$ this relation yields that for the transformed functions $C(\mathbf{k})$ and $g(\mathbf{k})$ one has that $g(\mathbf{k}) = C(\mathbf{k})/(1-\rho C(\mathbf{k}))$. If we are interested in the integral $\int g(\mathbf{r})d^3r$, that is, in the Fourier transform $g(\mathbf{0}) \equiv g(\mathbf{k} = \mathbf{0})$, we get in particular that

$$g(\mathbf{0}) = C(\mathbf{0})/(1 - \rho C(\mathbf{0})). \quad (29)$$

The new important step made in the work of Coniglio et al. (1977) was that, as can be appreciated intuitively, the average cluster size S in the system is simply given by

$$S = 1 + \int \rho g(\mathbf{r}) d^3r, \quad (30)$$

where the unity here represents the given initial object (with a center at, say, $\mathbf{r} = \mathbf{0}$). In Eq. (30) ρd^3r is the probability of finding an object center in the space element d^3r and $g(\mathbf{r})$ is essentially the percolation correlation function (Stauffer and Aharony 1992), that is, the probability that, if there are objects centers at $\mathbf{r} = \mathbf{0}$ and $\mathbf{r}$, they will be in the same cluster. From Eq. (30) one has then that $\rho g(\mathbf{0}) = S-1$ and thus using Eq. (29), one obtains that

$$S = 1/(1 - \rho C(\mathbf{0})). \quad (31)$$

Hence, knowing that at the threshold $S \rightarrow \infty$, one gets that $\rho_c = 1/C(\mathbf{0})$, and thus, in principle, “all that is left” is to calculate $C(\mathbf{0})$.

There are basically two approaches for the calculation of $C(\mathbf{0})$. The first one is immediately called for by Eq. (28), from which it is apparent that if another relation between $g(\mathbf{x}, \mathbf{y})$ and $C(\mathbf{x}, \mathbf{y})$ is known, one can solve both functions and then find the value of S . Such a relation can be derived from corresponding approximations. One of these approximations, known as the Percus–Yevick closure (Hansen and McDonald 1986), was used for the solution of the problem at hand. Since the application of this closure was of a limited success (DeSimone et al. 1986), and since it would require a deviation from the simple outline of our main argument regarding the rigorous derivation of ρ_c , it will not be detailed here. The conceptually simpler and physically more transparent approach to the problem can be attributed to the suggestion of Bug, Safran, and Webman in 1985 (Bug et al. 1985b). They were able to determine the initial terms in a (diagrammatic) series expansion of the form $C(\mathbf{0}) = \sum c_n \rho^n$ and to relate the initial coefficients to the concept of the excluded volume. This already enabled them to derive the trends in

the behavior of the thresholds. However, this use, of what one may call an order-by-order (or series) approach, did not yield (in that work) actual values for the thresholds. The full utilization of this order-by-order approach came in the works of Alon and coworkers in 1990 (Alon et al. 1990).

Turning to the utilization of the latter approach we noticed already that in principle, $C(\mathbf{0}) = 1/\rho_c$. However, in practice, this does not provide directly an accurate enough value for ρ_c from the rather short series that were obtained thus far. On the other hand, a more successful, albeit biased, approximation has yielded, as mentioned below, very accurate results (Alon et al. 1990). For the description of the latter we start then from Eq. (30) using the well-understood relation that we had considered before, that is, replacing ρ by $B = \rho V_{\text{ex}}$. Hence, the aim of the corresponding procedure was to determine the, by now, well-understood and well-characterized parameter B_c . Following the above, we can write S in terms of a power series of the form $S = \sum a_n B^n$, which is similar to the form used for the derivation of S by a power series of p in lattice percolation (Stauffer and Aharony 1992). In the present case, having the quantity $C(\mathbf{0})$, expressed as a power series of the form $C(\mathbf{0}) = \sum b_n B^n$, enables the comparison of the coefficients on both sides of Eq. (31), yielding then relations between the coefficients a_n and b_n . Here, for example, $a_0 = 1$, $b_0 = 0$, $a_1 = b_1$, $a_2 = b_2 + b_1 a_1$, $a_3 = b_3 + b_2 a_1 + b_1 a_2$, and $a_4 = b_4 + b_3 a_1 + b_2 a_2 + b_1 a_3$. Having these relations and implementing the fact that S has a universal critical behavior of the form of Eq. (3), and then that the $B \propto p_s$ relation in lattices is fulfilled, we get that

$$S \propto (|B - B_c|)^{-\gamma}. \quad (32)$$

One can fit the series of S to the behavior described by Eqs. (31) and (32), in order to find the value of B_c . Here one utilizes the assumption that γ is the well-established critical exponent for both lattices and the continuum as expected from universality (see section “[The Critical Behavior in the Continuum](#)”). Of course, the “only” input needed for the implementation of this procedure is then the determination of as many b_n

coefficients as possible, and a good extrapolation of S . However, the derivation of the coefficients b_n is not trivial and becomes more and more complicated with increasing n (Drory et al. 1991). So far these values of b_n have been determined up to $n = 5$ for permeable hyperspheres, yielding, however, very accurate values for B_c that are only a few % off the Monte Carlo estimates for corresponding $D = 2$ to $D = 6$ systems (Wagner et al. 2006). Similar successes for systems of elongated boxes (Drory et al. 1991) and hard-core–soft-shell cubes (Drory et al. 1994, 1995) have been already obtained. In spite of those achievements, further basic and computational developments in the study of this subject are called for as will be outlined in section “Future Directions.”

The Application of the Soft-Core Objects Model to Composites

The results that we have derived above were based on the V_{ex} and B_c concepts as well as on the overlap criterion for local connectivity of randomly placed permeable objects. This model is perfectly appropriate for the description of porous media (Hunt and Ewing 2009; Shakland and Waff 1974; Sahimi 1984; Balberg 1986; Balberg et al. 1984a; Engelman et al. 1983). In particular, it explains the zero-like percolation threshold in systems where the participating pores have extremely high or extremely low aspect ratio (Balberg 1986). This is to be expected directly from the corresponding very high V_{ex}/v ratios then, and the inverse relation of that ratio and the percolation threshold (see Eqs. (24) and (25)). The somewhat more complicated model of objects with a hard-core and a soft-shell, where the objects can only overlap in their soft-shells, provides the understanding of percolation between conducting particles in systems of interacting particles (Drory et al. 1995) and in many composites (Bauhofer and Kovacs 2009). The first case was found to be very helpful in explaining the non-monotonic dependence of the percolation threshold on the objects’ concentration in micelles and microemulsions with a permeable surfactant (Grest et al. 1986; Bug et al. 1985a). The second case, which applies to numerous composites, where the conduction between particles is by

tunneling, is even more intriguing and therefore will be described now in more detail.

To consider this latter case, which is of very wide interest (Bauhofer and Kovacs 2009), we call here the permeable objects, the soft-core (SC) particles, and the other type of objects, hard-core–soft-shell (HCSS) particles. Two SC particles are considered connected if there is some partial overlap between them (Balberg et al. 1988; Drory et al. 1994), while two HCSS particles are considered connected if there is a partial overlap between their soft-shells, but no overlap is allowed between their hard cores (Berham and Sastry 2007; Drory et al. 1995). Following the above difficulty in defining the connectivity (and thus in determining the value of x_c) in the case of interparticle tunneling, but considering the exponential decay of the tunneling conductance with distance, a natural and quite common approach to overcome the above difficulty is to map the tunneling-percolation problem onto the HCSS model. This is done by associating a soft-shell of thickness δ with the effective tunneling decay length d (Berham and Sastry 2007; Ambrosetti et al. 2008; Otten and van der Schoot 2011; Chatterjee 2011). On the other hand, the SC approach that ignores altogether the above problem was suggested for the CNT particles (Balberg 2012; Ahmad et al. 2006). The purpose of this discussion is to point out that, surprisingly, the very many data on the x_c values in such composites show that the SC approach accounts much better for them than the HCSS approach, even though we practically know only the content of the (hard-core) particles, x . In what follows we turn to explain the above, rather surprising, observation and provide a quantitative evaluation of the mechanism that is proposed below for that explanation. For the comparison of the experimental data with the SC and HCSS models, we recall the above suggested excluded volume argument (Balberg et al. 1984a). The basic relation that was given in Eq. (24) is associated with the B_c being the topological invariant (limited to the range of (0.7–2.8 in 3D) (Balberg et al. 1984a; Charlaix 1986; Balberg 1985)) that determines the onset of global connectivity in general, and the electrical conductivity, in particular. Correspondingly, N_c is the critical value of the uniform particle density that is required for the

achievement of this B_c . We recall that the excluded volume V_{ex} is defined for SC convex permeable particles of volume v as the volume around the center of a particle where the center of another particle has to be in order for two particles to partially overlap (Balberg et al. 1984a). For example, for spheres we saw that $V_{ex} = 8v$, while for an isotropic orientations distribution of large aspect ratio cylinders of length L and radius r ($\ll L$) we saw in Eq. (25) that $V_{ex} = \pi r L^2$ and $v = \pi r^2 L$ (Balberg et al. 1984a). Similarly, for such a uniform distribution of thin SC discs of radius a and thickness w ($\ll a$) $V_{ex} = \pi^2 a^3$ and $v = \pi a^2 w$ (Charlaix 1986; Balberg 1985). Approximating x_c here by $x_c = N_c v$ and applying Eq. (24) we find that for permeable cylinders

$$x_c \approx B_c r / L, \quad (33)$$

while for permeable discs, we get that

$$x_c \approx B_c w / a. \quad (34)$$

The common rough estimate for x_c in the HCSS models also uses relation (24) and a uniform N_c but it considers a “net excluded volumes” as follows. For cylinders of hard-core radius r and soft-shell δ , the net excluded volume is $V_{ex} = \pi(r + \delta)(L + \delta)^2 - \pi r L^2 \approx \pi \delta L^2$ (Berham and Sastry 2007), and since $x_c = N_c \pi r^2 L$ we get by applying Eq. (24) that (Balberg 2012)

$$x_c \approx B_c r^2 / L \delta. \quad (35)$$

Similarly, for discs of hard-core thickness s and soft-shell δ we get that $V_{ex} = \pi^2(a + \delta)^3 - \pi^2 a^3 \approx 3\pi^2 \delta a^2$ and $x_c = N_c \pi s a^2$, which yields that

$$x_c \approx B_c s / 3\pi \delta. \quad (36)$$

A more detailed and elaborated derivation that follows the latter model (Ambrosetti et al. 2010) yields that $x_c \approx (4/3)(s/a) / \{[(8 + \pi^2)[\delta/(2a)] + 8\pi[\delta/(2a)]^2\}$, which is, up to a second order corrections in δ/a , essentially the same as the simple result given by Eq. (36).

Comparison of the experimental data with the predictions of the HCSS model, we recall that the typical tunneling decay length in the composites,

d , is of the order of 1 nm (Dalmas et al. 2006; Balberg 2009a; Li et al. 2007; Hicks et al. 2009; Sichel et al. 1982). Starting with the simpler case of the disc-like graphene sheets (GSs) it is well justified to assume that $\delta \ll a$ and that $\delta \approx d$ (Eda et al. 2009; Fan et al. 2010; Tkalya et al. 2010). Now, since $s/\delta \approx s/d \approx 1$ (Stankovich et al. 2006; Pang et al. 2010) and $B_c = 1.8$ (Charlaix 1986), the result of the HCSS model (Eq. (36)) suggests that $x_c \approx 0.2$. This is at least *an order of magnitude larger* than the experimentally observed values (Tkalya et al. 2010; Stankovich et al. 2006; Pang et al. 2010). Even more serious is the fact that there is no dependence in Eq. (36) on the aspect ratio of s/a , that is of the order of 10^{-3} – 10^{-2} in GSs (Eda et al. 2009; Stankovich et al. 2006; Pang et al. 2010) and is expected and known to be the main cause for the low x_c values in them (Stankovich et al. 2006) as is also the case of the CNT composites (Berham and Sastry 2007; Ahmad et al. 2006; Bauhofer and Kovacs 2009). Indeed, a detailed comparison of the experimental data (Ambrosetti et al. 2010) with the results of the HCSS approach for graphene-based composites yielded the very exaggerated values of the order of 100 nm for the tunneling decay distance, d , while as pointed out above, d should not be larger than a couple of nanometers. On the other hand, Eq. (34) yields that $x_c (\propto s/a)$ is of the order of 10^{-3} – 10^{-2} which fits well the abovementioned experimental results.

Turning to the predictions of the HCSS model, as suggested for the CNT polymer composites (Ottewill and van der Schoot 2011; Chatterjee 2011; Ambrosetti et al. 2010; Yu et al. 2010), we note that r is of the order of 1 nm for the single wall CNTs (SWCNTs) while it is in the range of 5–50 nm for the multiwall CNTs (MWCNTs) (Yu et al. 2010). However, in both cases $L/r \approx 10^2$ – 10^3 (Bauhofer and Kovacs 2009; Yu et al. 2010). On the other hand, since $d \approx 1$ nm and $r/\delta \approx r/d$, the latter is in the range between 1 (for SWCNTs) and 100 (for MWCNTs). Hence, while for both SC and HCSS models (Eqs. (33) and (35), respectively) the expected (Berham and Sastry 2007; Ahmad et al. 2006; Chatterjee 2011) $x_c \propto r/L$ dependence is maintained, the dependence of x_c in the corresponding HCSS model (Eq. (35)) is

offset in the MWCNTs case by the factor of r/δ ($\approx r/d$). This renders, however, *an order of magnitude discrepancy* between the experimentally observed x_c values (see the many data in Bauhofer and Kovacs (2009) and the prediction of Eq. (35). Here, again then, the simple dependence of x_c on the aspect ratio (Eq. (33)) yields the lower values that are found experimentally (Bauhofer and Kovacs 2009). Indeed, the factor r/δ in Eq. (35) represents the excluding particle correlations (Drory et al. 1995) that become more dominant as one turns from the SWCNTs ($r/d \approx 1$) to the MWCNTs ($r/d \gg 1$). This larger discrepancy for the MWCNTs is quite an important observation here since it indicates that the general better approximation of the SC is due to the *diminishing exclusion of the particles positions* in real composites.

Following the above evidence for the a priori unexpected better approximation of the SC model for both types of composites we try now to explain it following the consensus of all the HCSS and SC models (Berham and Sastry 2007; Ahmad et al. 2006; Ambrosetti et al. 2008; Otten and van der Schoot 2011; Chatterjee 2011) that the basic property that brings about the low x_c values is the extreme aspect ratio of the carbon particles. The question that remains then is, what other property of these particles can minimize the correlations that are imposed by the hard cores of the particles. The answer to this question is the simple fact that in all these previous HCSS models the systems, as computer drawn in Fig. 10a, were assumed to consist of straight-rigid, nonpermeable, cylinders or discs. Correspondingly, by the removal of their rigidity constraint, the major limitation due to the correlations in the spatial arrangement of the hard cores can be eliminated. Hence, it is apparent that the particular property that eliminates correlations is that both CNTs (Kim et al. 2005; Dalmas et al. 2007; Fakhri et al. 2009) and GSs (Hicks et al. 2009; Stankovich et al. 2006; Chen 2011) are flexible. Indeed, this “bendability” feature of those particles (Biswas and Lee 2011) is well known and is probably the reason for the suggestions to base on them “flexible” (Chen 2011) or “stretchable” (Stankovich et al. 2006) electronics (Biswas and Lee 2011).

Turning to the above suggestion of how the bendability can overcome the rigidity assumed in the HCSS models let us consider a system of permeable sticks in a 2D system such as illustrated in Fig. 10a while in Fig. 10b we also show the corresponding basic conducting unit of the percolation backbone. This unit, which is the abovementioned singly connected bonds (Stauffer and Aharony 1992; Balberg 2009a, b), is a conducting particle that is in electrical contact with two other particles. As given in Eqs. (33) and (34) (Balberg 1985, 1986; Balberg et al. 1984a) in such systems as in Fig. 10, N_c is proportional to the inverse of the aspect ratio. Now assume that the “sticks” in Fig. 10 are not permeable but they are allowed to bend over each other at the otherwise “would be” intersections (say, under the random addition of permeable sticks). The distance between the axes of two of them is of the order of $2r + d$. Since the sticks are long ($L \gg r, d$) and the distance between consequent intersections with the given stick in the vicinity of the threshold should be of the order of L/B_c ($\approx L/3$), that is much larger than $2r + d$, this “long range” bending-over does not cause any significant change in the global topology of the system. The application to the CNTs case is



Principles of the Theory of Continuum Percolation, Fig. 10 An illustration of a small portion of a 2D system of permeable sticks (a) and the basic unit of the backbone of the percolation network. The latter consists of two sticks that intersect a third one (b). This basic unit is maintained for 3D systems of large aspect ratio, nonpermeable sticks, if the hard-core sticks slightly bend over each other, yielding a 3D geometry of intersecting-like soft-core sticks. That such bending does indeed take place in CNT composites is illustrated by the SEM image of two close (5 μm long) MWCNTs (c) (From Balberg 2012)

straightforward then, since very little flexibility (much below that is observed in real CNTs) is needed to fulfill this $L/3 \gg 2r + d$ condition. In Fig. 10c we show for illustration a typical bending over of two MWCNTs as found in all types of CNTs by various microscopic structural techniques (Kim et al. 2005; Dalmas et al. 2007; Fakhri et al. 2009). Hence, from the topological point of view, the bendability of the CNTs makes their composites indistinguishable from their permeable objects counterpart.

Similar considerations in Balberg (2012) show the same conclusion for composites that are based on (sheet like) graphene-polymer composites rather than long nanowires (such as CNTs) polymer composites. Hence, that, surprising, “non-physical” soft-core model is found to account much better than the hard-core-soft-shell model for the well-established experimental result of the low percolation thresholds in CNT and GS polymer composites. This is attributed to the long-range bendability of these particles thus making the soft-core model the much more amenable description of the percolation phenomena in the above-discussed systems.

The Critical Behavior in the Continuum

The Generalized Thresholds and the Critical Behavior in the Continuum

Now we turn to see how the abovementioned connectivity parameters play a role in the determination of the most important feature in the study of percolation systems, that is, the behavior of the various properties at the proximity to the percolation threshold. Following the fact that $B_c = \rho_c < V_{ex}$, we simply have the relation $B - B_c \propto \rho - \rho_c$. Hence, for B very close to B_c and ϕ very close to ϕ_c (which is the interesting “critical” range), we can, by following Eq. (23), further generalize this relation to conclude that

$$\phi - \phi_c \propto B - B_c \propto \rho - \rho_c. \quad (37)$$

This relation is a very important one from the practical point of view, since ϕ is the only parameter that one can determine readily in a given system. However, the requirement for small

$\phi - \phi_c$ values must be kept then in mind when the critical behavior is studied in continuum systems. In fact, another very important precaution has to be taken into account when studying the critical behavior as a function of $\phi - \phi_c$ is as follows. We saw above that in many systems (such as sedimentary rocks and cellular composites), ϕ_c could be very small. Hence, a small $\phi - \phi_c$ (with respect to unity) does not actually tell us about the proximity to the threshold and thus the parameter that one should consider is a normalized proximity to the threshold, such as $\phi_d = (\phi - \phi_c)/\phi_c$ (Balberg 2017). We note that the latter problem is not severe in lattices of the “practical” ($D = 2$ or $D = 3$) dimensions because p_{sc} and p_{bc} for all these lattices are larger than 0.12 (Zallen 1983) and thus a small $p_s - p_{sc}$ or $p_b - p_{bc}$ is enough to indicate the proximity to the threshold. On the other hand, as noted in Balberg (1986, 2017), the overlooking of the above two precautions is one of the reasons that when considering experimental results in the continuum, improper comparisons with lattice-like critical behavior have been suggested.

Following the above discussion on the transition from the soft-core to the hard-core case we also note that in the small $B - B_c$ limit, Eq. (37) covers all systems, including those where ϕ represents the hard-core fractional volume in partially permeable (hard-core/soft-shell) objects. This is easy to appreciate, since at the close vicinity of the percolation threshold, the ratio of the hard-core volume to the entire (hard-core and soft-shell) volume can be considered a constant and since we know that, as in the model of Zallen and Scher (1971), the relation given by Eq. (37) holds in the hard-core limit. Indeed, many computer simulations, on many continuum systems (Balberg and Binenbaum 1985; Gawlinski and Redner 1983; Gawlinski and Stanley 1981) where the systems are well defined (and ϕ_c can be approached much more closely than in the experimental studies on “real” systems), have revealed the critical behavior of lattices. This is quite an important realization when one tries to explain the critical behavior in composites, considering the fact that the systematic approach that we described above for the percolation thresholds relies only on systems with permeable objects.

From our above discussion, we can expect, however, the same critical behavior for all types of objects, and one may further conjecture that this is the case when other local connectivity criteria are applied. In fact, thus far all Monte Carlo simulations have confirmed these expectations (Balberg and Binenbaum 1985). We note, however, that a high precision study of ϕ_c and the critical exponents of a system of permeable spheres was claimed to indicate a small variations with respect to the corresponding lattice values of the same exponents (Rintoul and Torquato 1997). This conclusion can be contrasted by the rigorous exact mapping of the permeable circles system onto the fine grid lattice system that was demonstrated by McCarthy already in 1987 (McCarthy 1987). As of now, however, further work will be needed in order to determine whether the above small deviation is a matter of accuracy or proximity to ϕ_c (see the discussion following Eq. (37) above), or if there is still something more fundamental there, that has not been satisfactorily studied thus far.

The Rigorous Proof for the Phase Transition Behavior in Continuum Percolation

As mentioned already in section “The Critical Behavior of Percolation Clusters” the possibility to map exactly the lattice percolation problem on the Ising (two spins, $q = 2$) model has proven rigorously that the percolation behavior is a second-order phase transition. This mapping has also shown that the critical behavior that is characterized by the critical exponents accounts well for that behavior. However, while as we have seen above the same behavior with similar exponents have been expected and observed in continuum systems, a rigorous proof that the percolation behavior in such systems represents a bona fide second-order phase transition has been provided only in the late 90s of the previous century. This was done in a series of papers by Drory (1996a, b, 1997) who extended the lattice mapping of Fortuin and Kasteleyn (1972) and the off-lattice version of the Potts model (i.e., $q \neq 2$, see section “The Critical Behavior of Percolation Clusters”) to continuum systems. In Drory’s extension, one has a system of randomly distributed particles

each of which can have one of the q possible spin states. Each spin has then a position in the continuum and it interacts with other spins via a spin-dependent potential which is different for parallel and non-parallel spins. The spins can also be coupled to an external field which tends to align them in a chosen state. In that approach, one can express the average of any physical quantity in the model as an average over the corresponding configurations that arise from the above spin assignments. Now, while the average of that off-lattice Potts model (that considers the spins) considers many configurations, the percolation cluster has only a single spin configuration. For the mapping of this extended Potts model onto percolation, one considers, after all the calculations of the magnetic Potts model are completed, the limit of $q \rightarrow 1$ (as if all the spins have the same value). The averages are taken then in the thermodynamic limit, that is, where the number of particles in the system N , is very large. Finally, to “eliminate” the effect of the field, h , that “has aligned the spins” one considers the $h \rightarrow 0$ limit. Since the magnetization M is a quantitative measure of the proportion of spins that have that single spin state, this limit is the percolation analog of M , which corresponds then quantitatively to the proportion of particles that belong to the same cluster. This proportion is just the probability that a randomly selected particle belongs to this cluster, that is, to the percolation probability $P(\rho)$ where ρ is the uniform density of the particles in the system. The above-described procedure can be summarized by

$$P(\rho) = \lim_{h \rightarrow 0} \lim_{N \rightarrow \infty} \lim_{q \rightarrow 1} M. \quad (38)$$

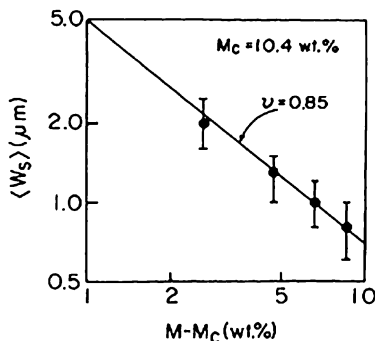
Similarly the average cluster size $S(\rho)$ is derived then from the susceptibility $\chi (= \partial M / \partial h)$ yielding that

$$S(\rho) = \lim_{h \rightarrow 0} \lim_{N \rightarrow \infty} \lim_{q \rightarrow 1} (\chi / kT). \quad (39)$$

Mathematically, as in the Potts lattice model (Potts 1952), the expressions derived by using these limits yield the classical definitions of the percolation probability (Wu 1978), $P = 1 - \langle 1/N \rangle (\sum s n_s) / N$. Here N is the number of particles in the system, s is the number of particles in the finite

clusters of size s , and n_s is the concentration of such clusters in the system. In other words, the Potts model that includes the spins has been “stripped” in Eqs. (38) and (39) of its magnetic properties without losing its character as describing a second-order phase transition. The important finding of Drory (1996a, b, 1997) was then that by using the above limits, he was able to show that for a random distribution of particles the result that was obtained previously for lattices (Wu 1982) is also obtained in continuum systems. Correspondingly, the critical exponents found in lattices should also emerge in the continuum.

Experimental Confirmations and/or Explanations of Experimental Results Probably the first experimental work that has demonstrated quantitatively the critical behavior of the geometrical-structural properties in the continuum, in particular that of the correlation length ξ was the statistical-structural analysis of Kapitulnik and Deutscher of discontinuous thin films of lead (Kapitulnik and Deutscher 1982). Since then following the developments of surface scanning methods there were quite a few similar studies (Toker et al. 2003). As an example, we show in Fig. 11 the result that was obtained by the Fourier transform analysis of the power spectra on various (conducting) contents of carbon black particles that were in embedded in a polymer matrix



Principles of the Theory of Continuum Percolation, Fig. 11 Dependence of the average cluster diameter of the conducting particles $\langle W_s \rangle$ on the carbon-black content as determined by the Fourier transform of the electrical noise power that was obtained on the corresponding composites. (From Balberg and Blanc 1985)

(Balberg and Blanc 1985). As seen in this figure the dependence of the average size of the conducting clusters $\langle W_s \rangle$ (that was derived by that method) on the carbon black content ($M = x$) in them, led to the critical behavior with the same value of the 3D correlation length exponent ν that was found for lattices (see section “The Critical Behavior of Percolation Clusters”).

Universal and Nonuniversal Behaviors of the Electrical Conductivity

As pointed out above, within the limited framework of this review, it will not be possible to consider all the many various dynamical properties (such as elasticity) that are determined by the added locally variable features in continuum systems and compare their behaviors with those derived for lattices. Correspondingly, we will confine our discussion to the property that is the most conspicuous, representative, and easiest to consider intuitively (Zallen 1983), and thus the most studied and applicable dynamical property, that is, the electrical conductivity (Balberg 2009b). It can be shown, as done by Rubin et al. in 1999 (Rubin et al. 1999) for the electrical noise, and by Berkowitz and Balberg (1993) for the liquid permeability, that the basic arguments associated with the critical behaviors of the other dynamical properties are similar in principle to those associated with the electrical conductivity (Octavio et al. 1988). This is despite the specific details associated with each of those properties.

In the previous sections, we saw that the main feature that makes continuum percolation an area of a much wider diversity and application, in comparison with what one finds in lattice percolation, is the wide range of systems that exhibit percolation thresholds. On the other hand, as far as the critical behavior is concerned, we have seen in Fig. 3 that the behaviors of the global geometrical-statistical properties are expected to be the same as those found in lattices. The question that arises then is whether the above behavior of the geometrical-statistical properties gives us a hint as to the critical behavior of the dynamical (or “physical”) properties of the systems in the continuum? A priori, since we saw that one can simply superimpose the conducting elements

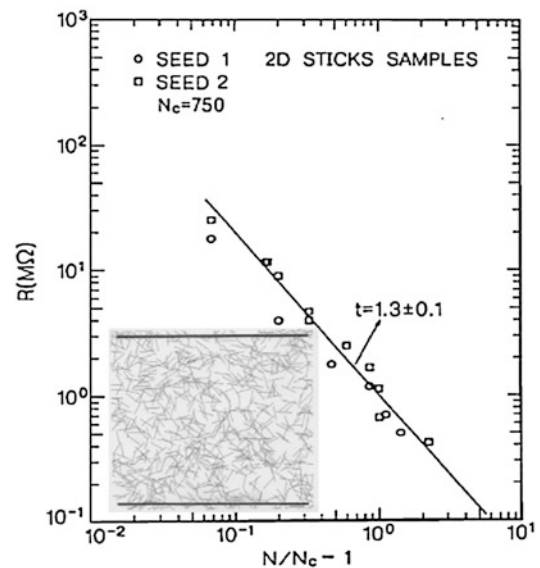
behavior on the geometrical-statistical behavior, we would expect now the same critical behavior as in Eq. (8), with the same exponent as in Eq. (10). The difference would rise then in the electrical properties of the conducting elements (see Fig. 6) which have no counter parts in the lattices. Turning to those “contact effects” let us consider the two possible features that are fixed in lattices, and may be random (or follow another distribution) in the continuum. This is easy to do by re-examining the system shown in Fig. 5 as a system of permeable circles. In this figure, we can see that the continuum randomness is manifested by the positions of the centers of the circles and the random-like degrees of overlap between two adjacent circles or spheres. If these circles are envisioned as pores filled with a conducting fluid (see Fig. 6), the latter degree determines the local resistance between a pair of them (Sahimi 2003; Balberg et al. 1988; Balberg 1986; Sen et al. 1985). This will yield a distribution in the resistance values of the actual resistors that connect pairs of pores in the system. The simplest approach to evaluate the contribution of the latter effect (that has no counterpart in lattice percolation) to the global conductance of the system is to assign a resistor, with a resistance value that is taken from the corresponding distribution, to an occupied bond. A more direct simulation of the system that involves also the random “implantation” of spheres has been shown (Balberg et al. 1988) to yield the predicted results that will be given below. The purpose of the following discussion is then to show how the corresponding distributions of the local resistance values can guide us to the determination of the critical behavior of the conductivity in “real” continuum systems.

Experimental Confirmations and/or Explanations of Experimental Results

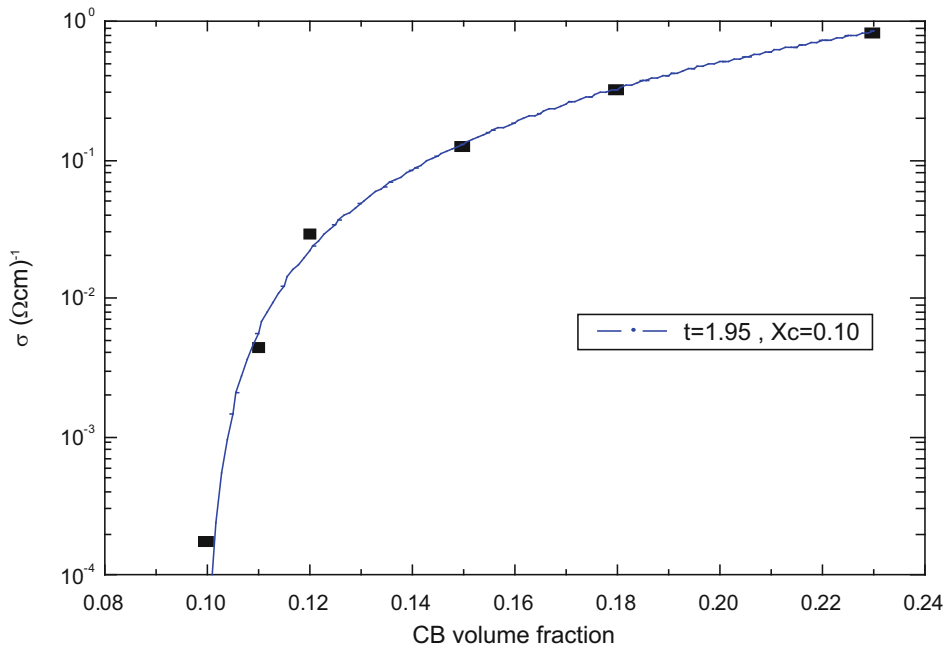
Indeed, in view of the universality of the percolation backbone (see Fig. 3) one does not foresee too much of a surprise here and a “universal” (lattice like) behavior of the conductivity is expected when all the resistors in the system are the same or the average of their resistance values is independent of $(\phi - \phi_c)$ or $(x - x_c)$. This explains the finding of a universal value t_{un} for t in many

“real” systems (Vionnet-Menot et al. 2005; Balberg et al. 1991; Bauhofer and Kovacs 2009; Balberg and Bozowski 1982; Abeles et al. 1975a). One of the first experimental confirmation of the universal critical behavior in a 2D continuum system was that of conducting line-segment drawing, where the sample’s resistance was measured as a function of the concentration N of the equal length segments. Presenting the data obtained, on a log-log scale, as shown in Fig. 12, revealed the 2D universal critical exponent $t_{un} = 1.3$.

An example of an experimental confirmation of the above universal behavior of the conductivity ($t \approx 2$) in a 3D polymer composite is shown in Fig. 13. In this system of a disordered collection of elongated carbon black particles that are entangled with each other (Balberg 1987a), there is a constant contact resistance between touching particles for which the description of the backbone, as illustrated in Figs. 2 and 3, applies. Hence, the lattice-like universal critical behavior of the conductivity is fulfilled.



Principles of the Theory of Continuum Percolation, Fig. 12 The dependence of the sample’s resistance as a function of the concentration of conducting line segments in a 2D system. These results were obtained by a computer driven experiment where the segments were drawn by a pencil and the resistance were measured by an Ohmmeter. (From Balberg et al. 1991)



Principles of the Theory of Continuum Percolation, Fig. 13 The measured dependence of the electrical conductivity on the carbon-black (Ketjenblack, high structure)

particles content in a carbon-black-polymer composite. (From Ravid 2012)

Let us turn now to the cases where the resistors in the system are, as exhibited in Fig. 6, more intimately associated with its continuum nature. As we noted already, while there were a variety of confirmations of nonuniversal behaviors in continuum system it took 6 years, until the “missing link” of the above 1979 “toy” distribution of K&S (see section “The Percolation Behavior of the Electrical Conductivity”) and its application for “real,” or continuum, systems was made by Halperin, Feng, and Sen in 1985 (Halperin et al. 1985). Thus, attention was finally given to the results of K&S that can be considered the cornerstone of the field of “nonuniversal” behavior of the dynamical properties in the continuum. What apparently took these 6 years in order to understand, even in principle, the emerging numerous experimental observations of nonuniversal t values in the 1970s and 1980s (i.e., the $t \neq t_{un}$ relation, see Eq. (19)) (Balberg 1987a; Pike 1978), was the need to find a distribution function of the resistors values in a given “real,” natural or artificial, system. The breakthrough of the work of Halperin et al.

(1985) was their ability to show that in sedimentary rocks the values of the local resistors are essentially distributed according to the “toy model” function of K&S. In fact, as will be emphasized along this part of the review, the determination of the resistors distribution function is the crucial step for the understanding of the critical behavior of the electrical conductivity (or other dynamical properties (Balberg et al. 1988)) in a given continuum system. The basic physics of this key issue, that has not been systematically reviewed previously, will be described below in some detail.

The Local Resistors and Their Value Distribution in Some Continuum Systems As mentioned above, the conductors’ distribution as given by K&S was considered to be quite an abstract one until their resistors value-distribution was suggested for some real systems by Halperin, Feng, and Sen in 1985 (Halperin et al. 1985). Once this distribution is given, its mapping onto the K&S distribution is, as shown below, quite straightforward (Balberg 1998). A more

transparent way to derive the corresponding critical behavior was based on the use of a physically rigorous approach (Feng et al. 1987; Rubin et al. 1999). The corresponding findings were the very crucial steps that have finally explained the basis for the universal and nonuniversal behaviors of “real” systems. In passing, we note that a posteriori, the critical behavior estimated by the above consideration of $\langle r_c \rangle$ (see Eq. (17)) was also confirmed by the latter approach (Rubin et al. 1999). It should be emphasized throughout that while the model of K&S was based on lattice-like p and p_c probabilities, in the continuum we simply replace p and p_c by ϕ and ϕ_c or x and x_c . This as we have shown above is clearly justified when $\phi \rightarrow \phi_c$ (Balberg et al. 1988) or $x \rightarrow x_c$ (Balberg 2012; Balberg et al. 2016) (see Eq. (37)). Since both approaches have been given in detail in the literature, we will only outline here the principal steps in their utilization for the determination of the corresponding t values. For brevity, let us assume that the resistance of a local resistor in the system, $1/g$, is determined by a single local geometrical parameter, ε , and that the distribution of the ε values in the system, $h(\varepsilon)$, is known. The distribution function of the local conductor values, $f(g)$, is simply given then by Balberg (1987a, 1998)

$$f(g) = h(\varepsilon)(d\varepsilon/dg). \quad (40)$$

“All one has to do” in order to find the $f(g)$ distribution is to derive the function $h(\varepsilon)$ from the local configuration that occurs in the system (which is usually not easy to do, see below) and the function $\varepsilon(g)$ (which is usually easy to do). To illustrate this procedure and its consequences we reconsider the three principal local configurations that were studied in detail. These three configurations are illustrated in Fig. 6, where the “conducting” phase is colored in red and the “insulating” phase is colored in yellow. Starting from the random void (RV, sedimentary rock-like system (Feng et al. 1987), or a metallic bulk in which holes were punched out (Last and Thouless 1971)), that is also known as the Swiss cheese-like system, we can assume that the distance between the surfaces of the spherical pores is ε , and there is

a “neck” of volume $(2\sqrt{b\varepsilon})C_D\varepsilon^{D-1}$ between them. Here, b is the radius of the insulating pores and C_D is a constant (which is 1 in $D = 2$ and $\pi/4$ in $D = 3$). This volume determines the resistance of the neck that is associated with two adjacent spheres (Halperin et al. 1985), since beyond (or outside) this “neck” the local resistance in the system is relatively small. The value of the local resistor in the system is well approximated then by the resistance of the “neck” which is given by $\rho_0((2\sqrt{b\varepsilon})/C_D\varepsilon^{D-1})$, where ρ_0 is the resistivity of the embedding conducting medium. Hence, the local conductance can be expressed by $g \propto \varepsilon^{D-3/2}$.

In the second configuration, known as the inverted random void (IRV) system, the overlap between two spheres with a radius b can be characterized by the parameter $\varepsilon = 2b - r$, where r is the distance between the centers of the adjacent spheres. Such systems include granular metal above the onset of metallic conductivity (Fonseca and Balberg 1993) and systems of pores filled with a conducting liquid (Berkowitz and Balberg 1993; Feng et al. 1987; Balberg et al. 1988). In that IRV configuration, the neck for conduction is approximated to be $2\sqrt{b\varepsilon}$ long, and it has a cross section of $C_D(b\varepsilon)^{(D-1)/2}$ ($C_D = 2$ in $D = 2$ and $C_D = \pi$ in $D = 3$), yielding that $g \propto \varepsilon^{D/2-1}$. For the above two cases we have then that $g \propto \varepsilon^m$, where $m = D-3/2$ in the RV model and $m = D/2-1$ in the IRV model (Balberg 1998).

The third case is that of conduction between two spheres that do not overlap and for which the distance between their centers is r and the distance between their surfaces is $r-2b$. In that case, the conduction between the two spheres, if carried out by tunneling, is possible, due to the charge transfer probability between the surfaces. This probability is expected to decrease as $\exp.[-2(r-2b)/d]$, where d is the effective (say, the WKB) tunneling decay coefficient (Balberg 1987a). This percolation-tunneling (PT) case will be further considered in some detail in the following paragraph in view of its being of wide interest in condensed matter physics and materials science.

Let us start then with the corresponding $h(\varepsilon)$ and $f(g)$ distributions in the RV and IRV cases. Noting that the theoretical and/or the experimental derivation of these distributions is the most difficult

part in the present problem, one can consider the first suggestion of a “real” $h(\varepsilon)$ dependence (and its use in the present context) as the breakthrough in the evaluation of $f(g)$. This breakthrough that led to the understanding of the nonuniversal behavior of the dynamic properties in continuum systems was achieved, in the work of Halperin et al. (1985) who showed that in porous media $h(\varepsilon)$ becomes a constant, h_0 , as $\varepsilon \rightarrow 0$. The corresponding distribution is, however, normalizable since $h(\varepsilon)$ tapers off with increasing ε above a certain value of ε (as is obvious from the finite size of the system). Being interested in the smallest ε values, that is, the largest resistors in the system, one can easily apply the “recipe” given by Eq. (40). Using then the general $g \propto \varepsilon^m$ relation, where m is the relevant exponent, we have that $f(g) \propto dg/d\varepsilon \propto h_0 g^{(1-m)/m}$ and thus (see section “The Percolation Behavior of the Electrical Conductivity”), that the α value of K&S is $1-1/m$. In the above RV case, for which $m = D-3/2$, we have then that $t-t_{un} = \alpha/(1-\alpha) = m-1 = D-5/2$. Hence, from the K&S model (see Eqs. (15), (16), (17), (18), and (19)) it is easy to conclude that for $D = 2$ a universal behavior will be found (since $\alpha < 0$) while for $D = 3$, a value of $t-t_{un} = 1/2$ is predicted, as confirmed indeed by the corresponding simulations of Sen, Roberts, and Halperin in 1985 (Sen et al. 1985).

The above procedure was generalized by Balberg in 1998 (Balberg 1998) for any power law distribution of the $h(\varepsilon) \propto \varepsilon^{-\omega}$ type which, following the above, yields that $f(g) \propto g^{(1-m-\omega)/m}$ and correspondingly (see Eqs. (18) and (19)) that $t-t_{un} = (m + \omega - 1)/(1 - \omega)$. Of course, we note that we must have that $\omega < 1$, so that the distribution is normalizable. For the three dimensional RV case we will generally get then that $t-t_{un} = (D-5/2 + \omega)/(1 - \omega)$. It is important to note that if ω varies from one ε range to another, the behavior obtained will be more complicated. A mapping similar to the one of the RV model was obtained for the IRV model (Balberg et al. 1988; Balberg 1998) yielding that for $D \leq 4$, $\alpha < 0$, and thus the divergence of the conductance is obtained (for the $\omega = 0$ case) only for $D \geq 5$.

One can derive however these results in a physically more transparent and rigorous manner

(Feng et al. 1987; Rubin et al. 1999; Halperin et al. 1985) by starting from the LNB model. Then one finds the relation between the parameter ε , that is relevant to the value of the resistors, and its dependence on the proximity parameter $p-p_c$, so that a relation such as that of the K&S model is found between the average local resistance $\langle r_c \rangle$ and $p-p_c$. For the $\varepsilon \rightarrow 0$ limit, which corresponds to the larger $1/g$ resistors (that must be included in the network when $p \rightarrow p_c$), we assume, as above, that $h(\varepsilon) = h_0$ and that $g \propto \varepsilon^{-m}$. The corresponding $\langle r_c \rangle$ is determined then by

$$\langle r_c \rangle \propto \int_{\delta}^{\Delta} h_0 \varepsilon^{-m} d\varepsilon; \quad (41)$$

where Δ is the ε value above which $h(\varepsilon)$ tapers off with increasing ε , and δ is the smallest ε value (which is associated with the smallest g value), in a typical link, that is made of L_1 singly connected bonds. The probability that ε will be larger than a given δ for a bond in this link is simply $1 - \int_0^{\delta} h_0 d\varepsilon$, and thus for all L_1 bonds in the link it is $(1 - \int_0^{\delta} h_0 d\varepsilon)^{L_1} = \exp(-\delta L_1 h_0)$. This means that at $\delta \approx 1/L_1 h_0$ this probability starts to become significantly smaller than unity, and thus this relation provides a good estimate of δ , which is $\delta \propto 1/L_1$. Having this value and considering that $\delta \ll \Delta$ and that $m > 1$ (see above), we get from Eq. (41) that

$$\begin{aligned} \langle r_c \rangle &\propto h_0 \delta^{-m+1} \approx h_0^m L_1^{m-1} \\ &\propto (p-p_c)^{1-m}; \end{aligned} \quad (42)$$

This result yields, as above (see Eqs. (18) and (19)), that $t = t_{un} + (m-1)$. As we saw for the RV model, $m = D-3/2$, and thus for the corresponding 3D system we get $t = t_{un} + 1/2$, in accordance with the above result that was obtained from the K&S model. Similarly, for the IRV model we got that $m = D/2 - 1$, and thus for $D = 3$, we have that $m < 1$ and $\alpha < 0$ yielding that $t = t_{un}$. We can further attach the distribution term $\varepsilon^{-\omega}$, as above, and get that instead of the relation of $\delta L_1 h_0 \approx 1$ we will have that $\delta^{(1-\omega)} L_1 h_0 / (1-\omega) \approx 1$. Hence, in the more general case, $\langle r_c \rangle \propto h_0 \delta^{-m + 1 - \omega} \approx h_0^m L_1^{(m + m-1)/(1-\omega)} \propto$

$(p p_c)^{-(\omega + m - 1)/(1 - \omega)}$ or $t = t_{un} + (m + \omega - 1)/(1 - \omega)$ (Balberg 1998). As an example of the confirmation of the above prediction, we show in Fig. 14 the results of simulations for the case of permeable spheres in the IRV configuration. As seen in the figure, the predicted universal behavior for $D = 3$ and the nonuniversal behavior for $D > 3$ are well confirmed. In this figure we also show the simultaneously derived behavior of the electrical noise which as predicted for that dynamical property, will exhibit a nonuniversal behavior (Balberg et al. 1988). We further note that, as predicted (Balberg 1998), the deviation from the universal behavior increases with D .

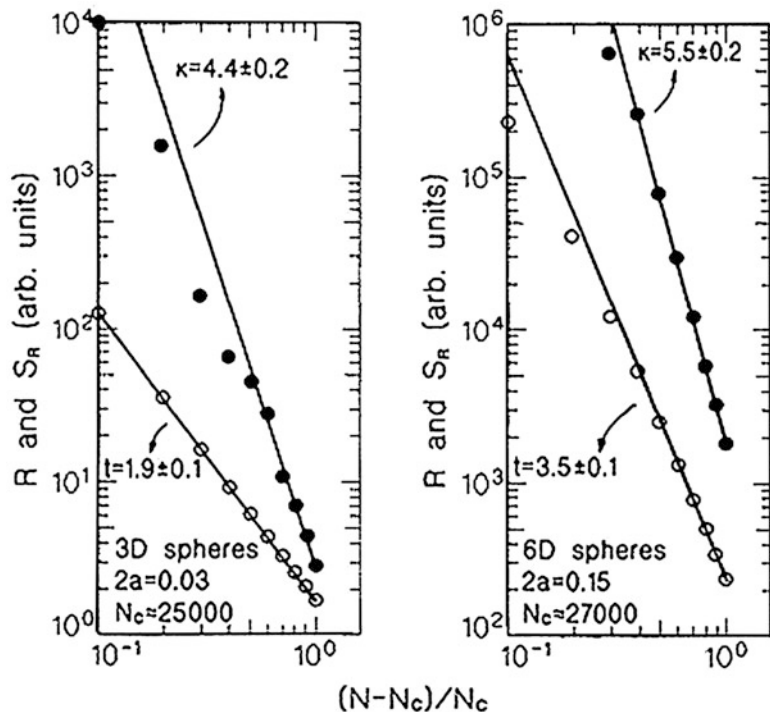
The Tunneling Percolation Problem

Before turning to the problem of the average value of the local resistor and thus to the value of t in the case of tunneling percolation (PT in Fig. 6), let us examine the unique relation between tunneling and percolation (Balberg 1987a; Johner et al. 2008). Tunneling is essentially the principal mechanism of electrical conduction in most classes of composite materials. In contrast with the

RV and IRV cases, the tunneling behavior is due to a coupling between the geometry and a physical mechanism. As one considers the tunneling in the percolation-systems context, one notices that it challenges our above understanding of continuum percolation as follows. In lattices (S&Z-like), or in the above RV and IRV systems, the geometrical connectivity and the electrical connectivity are very clear and both are associated with the geometrical continuity of the conducting phase. This is also the case when we define a soft-shell that wraps the hard-core so that the overlaps of the soft-shells provides a continuous conducting phase, as can be envisioned to be the case in microemulsions (Grest et al. 1986; Bug et al. 1985a). When the conductivity is provided only by tunneling, there is no geometrical connectivity (or continuity) but there is electrical connectivity. Since, in principle, the tunneling range of “interaction” between two particles is infinite, that is, the system is a priori always above the percolation threshold, one has to determine first a relevant percolation threshold, and only then evaluate the critical behavior. The latter connectivity, however,

Principles of the Theory of Continuum Percolation, Fig. 14

The dependence of the sample resistance R (open circles) and the relative resistance noise S_R (filled circles) on the concentration of the implanted spheres in 3D and 6D inverted random-void systems. The derived exponents are given in the figure. (From Balberg et al. 1988)



is problematic, since all the conducting objects are connected electrically to each other (albeit with a different “strength” that is determined by the exponential decay of the tunneling probability). Hence, the system has a “zero span” of the geometrical connectivity and an “infinite span” of the electrical connectivity. It appears then to be quite surprising (Balberg 2002) that systems (such as many types of composites) that belong to this “counter” percolation scenario exhibit computational (Balberg et al. 1990; Johner et al. 2008) or experimental (Vionnet-Menot et al. 2005) well-defined percolation thresholds and a universal or a nonuniversal critical behavior. Indeed, until quite recently the very many experimental or computational studies on numerous composite systems that were discussed in terms of a bona-fide percolation critical behavior have done so with no justification.

The first explanation for the above paradox was given only very recently by Toker et al. in 2003 (Toker et al. 2003). They concluded by examining the fractal dimension of the “electrical” percolation network (that was derived by a local electrical probe microscopy on real composites) that if the tunneling decay parameter is very small compared with the size of the objects (say, spheres) the electrical network that exists in practice, consists only of adjacent neighbors. Hence, that network determines the global measurable conductivity of the system of these neighbors. In that case the percolation threshold is simply associated with the concentration of “near neighbor” objects, such as in the case of a system of conducting objects which have a “large” hard-core and a thin soft-shell of a constant thickness d . In that case, the percolation-tunneling problem can be mapped onto such a model. The dynamical properties are determined then, in general, by the local resistors distribution as in the above given IRV-related discussion of microemulsions (Grest et al. 1986; Bug et al. 1985a).

When this is not the case, that is, when the tunneling distance is of the order of the size of the conducting objects, such as the case in granular metals (Abeles 1976; Toker et al. 2003; Balberg et al. 2004) or quantum dot semiconductors embedded in a dielectric (Balberg et al. 2007),

the observation of a percolation threshold and a critical behavior is less obvious. This is since in those cases there will be a contribution of both, tunneling to the nearest neighbors and the tunneling to farther neighbors. It turns out that the solution to this problem can be based on the same model as in the above case if one takes into account the information that one has on the radial distribution function (RDF), $G(r)$, of a collection of, say, hard spheres. This function is defined (Ziman 1979) as the probability $G(r)dr$ to find a particle center within the r and $r + dr$ distance interval from a given particle. The function exhibits, however, an “evolution” of the peak of “nearly touching” particles as one follows its variation from the dilute, or the small b , limit to the (hard-core) dense spheres limit, that is, as the particles size and/or their density increases. In particular, the common conclusion of all the corresponding models is that the larger the phase content of the conducting particles (i.e., the particles density and/or their size) the narrower the “tail” of the near neighbors separations (Kirkpatrick 1973). This is equivalent in the present context to the statement that more particles will overlap their neighbors within a shell of thickness d . In other words, the way the hard spheres arrange themselves in the case of the dense limit yields a preferred conduction network that can be presented by a model that is much like the one proposed above for the $b \gg d$ case. On the other hand, it is of course appreciated that as the system becomes very dilute it is reminiscent of the near-neighbor hopping model (Shklovskii and Efros 1984). Indeed (as shown in section “Further Extensions for Various Off-Universal Conductivity Exponents in Continuum Systems”), a close examination of the dependence of the conductivity on the conducting phase content in granular metals (Balberg et al. 2004) reveals a density regime in which both percolation and hopping can simultaneously account for the experimental data. In contrast, a percolation-only model can account for the data obtained on the abovementioned “large spheres” systems such as Carbon black-Polymer composites (Balberg 2009a; Rubin et al. 1999; Toker et al. 2003). A summary of the above conclusions as derived in Toker et al. (2003) by a

comparison of electrical microscopy results that were obtained on the two extreme systems that were described above is presented in Fig. 15.

Let us start then our evaluation of the critical dependence of the conductivity with the simplest percolation tunneling model, that is, when we consider only the distance distribution of the nearest neighbors as appears to be given by the RDF (Shklovskii and Efros 1984). The corresponding problem of the average local resistance in the tunneling-percolation problem was solved thus far accurately only for 1D (or quasi 1D, see below) systems (Balberg 1987a, b). At higher dimensions, the lack of analytic expressions for the $f(g)$ distribution does not enable a simple evaluation of the corresponding critical behavior. However, with the information already available (Ambegaokar et al. 1971; Torquato et al. 1990) it is possible, as described below, to obtain a good physical understanding and derive semi-quantitative results for the critical behavior (Johner et al. 2008). We consider then the simple case of a linear chain of geometrically, but not electrically, isolated “metallic” spheres (Grimaldi et al. 2003) with a hard-core radius b in a system where the average distance between them is $2a$ ($= 1/N_1$, where N_1 is the average number of spheres per unit length). The random distribution of the distances of the centers of the nearest neighbor

spheres from a given sphere center in the corresponding 1D system is the well-known 1D Hertz distribution (Shklovskii and Efros 1984; Balberg 1987a, b) that can be written as (Balberg et al. 2004).

$$h_1(r) = [1/(2a - 2b)] \exp [-(r - 2b)/(2a - 2b)], \quad (43)$$

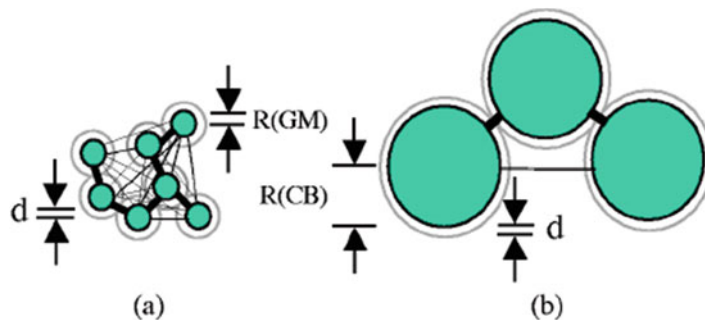
where r is the distance from the center of the reference sphere. On the other hand, the local tunneling conductance between two such spheres is simply given by

$$g = g_0 \{ \exp [-2(r - 2b)/d] \} \quad (44)$$

where g_0 is a corresponding geometrical-physical constant and $2/d$ is the tunneling probability decay constant. For the calculation of the average value of the local resistance let us neglect the resistance between “non-adjacent” spheres, that is, we assume that $b \gg d$. Applying Eqs. (40), (43), and (44), one gets that for the nearest neighbor connections (or bonds (Balberg 1987a, b; Balberg et al. 2004)).

$$\begin{aligned} f_1(g) &\propto \exp [2(r - 2b)/d] \\ &\times [1 - d/2(a - b)] \\ &\propto g^{-\alpha}, \end{aligned} \quad (45)$$

where,



Principles of the Theory of Continuum Percolation, Fig. 15 An illustration of small parts of two types of composites. The circles represent the conducting particles and their tunneling shell which has a width d . The thick segments represent the tunneling connections between nearest neighbors, while the thin segments represent tunneling connections to farther neighbors. The relation

between the size of the particles and the tunneling range is illustrated for granular metals in (a) and for spherical carbon black particles in (b). (From Toker et al. 2003). Note the ratio between the tunneling distance d , the size of the particles R and the participating neighbors in the conducting networks

$$\alpha = 1 - d/4(a - b). \quad (46)$$

Following the above K&S prediction (Eq. (19)) for the exponent t , one has, when assuming that $4(a-b) > d$, that

$$t - t_{un} = 4(a - b)/d - 1. \quad (47)$$

This finding has been adopted not only for the relatively simple 3D cases where the above $h_1(r)$ distribution is still appropriate (Johner et al. 2008) to general 3D random systems as follows.

While the above results (as shown below) contain the essence of the behavior of 3D systems one would like to derive the value of t for the “full” 3D systems while noting that the 3D Hertz distribution, in its simplest form, is proportional to $\exp. [-(r/2a)^3]$ (Shklovskii and Efros 1984; Ambegaokar et al. 1971). It turns out that unlike the 1D case, the t value (or the α value) is not a constant and it has a $t(\rho)$ dependence (Johner et al. 2008). Here ρ is the density of the particles (say, spheres) and the total fractional volume % of the particles x is given by $x = \rho v$, where v is the volume $(4\pi/3)b^3$ of a hard-core spheres.

To consider the 3D behavior let us use the 1990 (Torquato et al. 1990) result of Torquato, Lu, and Robinstein for the 3D distribution function of the interparticle distances of the first nearest neighbor spheres, $h_3(r)$. The latter result can guide us in predicting the behavior of the more general $D > 1$ systems. The relevant dominant term that is implied by their $h_3(r)$ is

$$H_3(r - 2b) \propto A(\rho)(r - 2b)^2 \exp \left\{ -[8 A(\rho)/b^3] [r^3 - (2b)^3] \right\}, \quad (48)$$

where $A(\rho) = [\rho v(1 + \rho v)/(1 - \rho v)^3]$. This density ρ is related to the above $2a (> 2b)$ parameter (i.e., the average distance between the sphere-centers of two nearest neighbors) that we simply define here by $\int_{2b}^{\infty} h_3(r)dr$. A very rough, but geometrically more transparent, estimate of the average interparticle distance $2a$ (which is enough for the present discussion of the basic physics of the problem) can be given by assuming that the spheres are implanted randomly (as in the $a \gg b$ case). In this case a is associated with

the average “territory” of a sphere and is thus given by the simplified relation

$$(4\pi/3)a^3\rho = 1. \quad (49)$$

Returning to Eq. (48), we can follow the behavior of $f(g)$ by applying Eqs. (40), (44), and (48) in a way that yielded Eq. (45). The first feature that we encounter in $H_3(r-2b)$, and which has no counterpart in $h_1(r-2b)$, is a peak at some r_m that is of the order of $2(a-b)$. For $r < r_m$, both $H_3(r-2b)$ and the resistance term $1/g \propto \exp.[2(r-2b)/d]$ increase with increasing r and thus $f_3(g)$ is increasing with $1/g$. The rate of this increase may be very large for the small $r-2b$ values due to the dominance of the $(r-2b)^2$ term in Eq. (48) that can be translated to a $g^{-\alpha}$ behavior with $\alpha > 1$ for a limited g range, in some cases (Balberg 2009a). To derive then the conspicuous features of the $\alpha(\rho)$ dependence in a transparent way one can use a simplified version of the $H_3(r)$ function that describes rather accurately the distribution of nearest neighboring particles in the low density regime (Johner et al. 2008) which is actually a generalization of the $b = 0$ case of the well-known Hertz distribution (Shklovskii and Efros 1984)

$$P(r) \approx 3r^2/(2a - 2b)^3 \exp \left\{ -[(r^3 - 2b)^3/(2a - 2b)^3] \right\}, \quad (50)$$

where $r \geq 2b$, and $2a$ is the approximate (or the average) distance between the centers of nearest neighboring spheres. The application of this $P(r)$ within the framework of the Effective Medium Approximation (EMA) for the bond percolation problem has enabled Johner et al. (2008) to get (for not too-close to the threshold) an analytic expression for $\alpha(\rho)$. Considering then the above-mentioned relation of $p_b = p_s^2$ (see Eq. (1)) in lattices and the $x = fp_s$ relation of Scher and Zallen they finally obtained that

$$t(x) = t_{un} + [4(a - b)/d]\mathcal{F}(1 - x_c^2/x^2), \quad (51)$$

which for a corresponding $\mathcal{F}(x)$ function is an expression that is amenable for comparison with

experimental results. We note here that the pre-factor of $\mathcal{F}(x)$ is the same as in the 1D case and thus the role of the $\mathcal{F}(x)$ function is just to describe the variation of the amplitude of $t(x)$ as a function of x . Hence, in view of the above, the transitions from a nonuniversal behavior to a universal behavior seem to be well understood and well accounted for, semi-quantitatively. However, further work is needed in order to examine the 3D effect more quantitatively. The following understanding of the conductivity staircase phenomena in the continuum is clearly a step in this direction.

The Percolation Conductivity Staircase in the Continuum

We have suggested in section “[The Percolation Behavior of the Electrical Conductivity](#)” that in some systems there is a geometrically induced hierarchy of local conductivities so that the behavior can be described in terms of a lattice-like model that can be called the tunneling percolation staircase model (Balberg et al. 2013, 2015). Following that general discussion on the possibility of a staircase behavior of the conductivity this behavior is also expected to take place due to various tunneling distances in a given system. In particular, it is expected that the dependence of the conductivity on the metallic fractional volume content in granular metals, $\sigma(x)$, can be analyzed in terms of a few subsequent percolation transitions that are associated with corresponding interparticle tunneling transport. Indeed, such a behavior was found in nanogranular Ag–Al₂O₃ (Balberg et al. 2013, 2015) and nanogranular Ag–SnO₂ (Wey and Li 2013) systems. However, examining those experimental data one may argue that the presence of the conductivity stairs in these two independent reports was inconclusive since the claimed stairs may just reflect experimental fluctuations in the measurements. In contrast, recent experiments have confirmed the validity of the attribution of the stairs to the tunneling conduction (Wey and Li 2013). Hence, for composite materials we can present the macroscopically measured conductivity by

$$\Sigma\sigma_i(x) = \Sigma\sigma_{i0}[(x - x_{ci})/(1 - x_{ci})]^t, \quad (52)$$

for $x_{ci} \leq x \leq 1$, where x_{ci} is the conductivity threshold of the i th stair that is defined as the $x_{ci} < x < x_{c(i-1)}$ range (taking for completeness $x_{c0} = 1$ (Balberg et al. 2013)). σ_{i0} here is a constant ($\sigma_{i0} = 0$ for $x < x_{ci}$) and it is assumed that $\sigma_{i0} (\gg \sigma_{(i+1)0})$ and that it is proportional to the local conductance between a given particle and its i th nearest neighbor, $g_i (\gg g_{i+1})$. The exponent t here is the universal exponent of the conductivity (~ 2 in three dimensions) which is well established to be the same for lattices and the continuum (see section “[The Percolation Behavior of the Electrical Conductivity](#)” and the above discussion) for nearest neighbors. In the tunneling percolation model, $\sigma_{i0} \propto g_i = g_0 \exp[-2(\ell_i - 2b)/d]$, where g_0 is a constant, ℓ_i is the distance between the centers of two conducting particles (assumed to be spheres with diameter $2b$) and d is the tunneling decay length. Correspondingly, ℓ_i is associated with the its near neighbor site in the lattice (Balberg et al. 2013), or by the i th peak of the radial distribution function (RDF) of the particles in the continuum that was mentioned above (Ziman 1979; Torquato et al. 1990). Hence, a behavior similar to the one in lattices (see Fig. 4) is to be expected in corresponding systems in continuum.

Experimental Confirmations and/or Explanations of Experimental Results In order to set the stage for the full manifestation of the tunneling-induced staircase behavior let us examine the experimental $\sigma(x)$ dependence as observed on two granular metal systems (GMs). This is done in Fig. 15 where we see two conductivity stairs in the upper panel and a single stair in the lower panel. As seen here and as established previously, for both GMs (Abeles 1976; Abeles et al. 1975a), percolation thresholds at $x \approx 0.5$ and a universal critical behavior for $x > x_c$ have been found. The annealing that led to the results shown in the lower panel in this figure reflect the coalescence of the grains, so that one has there a continuous percolation network of fused grains that is consistent with the basic conjecture of S&Z (Scher and Zallen 1970) (see however Balberg and Binenbaum 1987a).

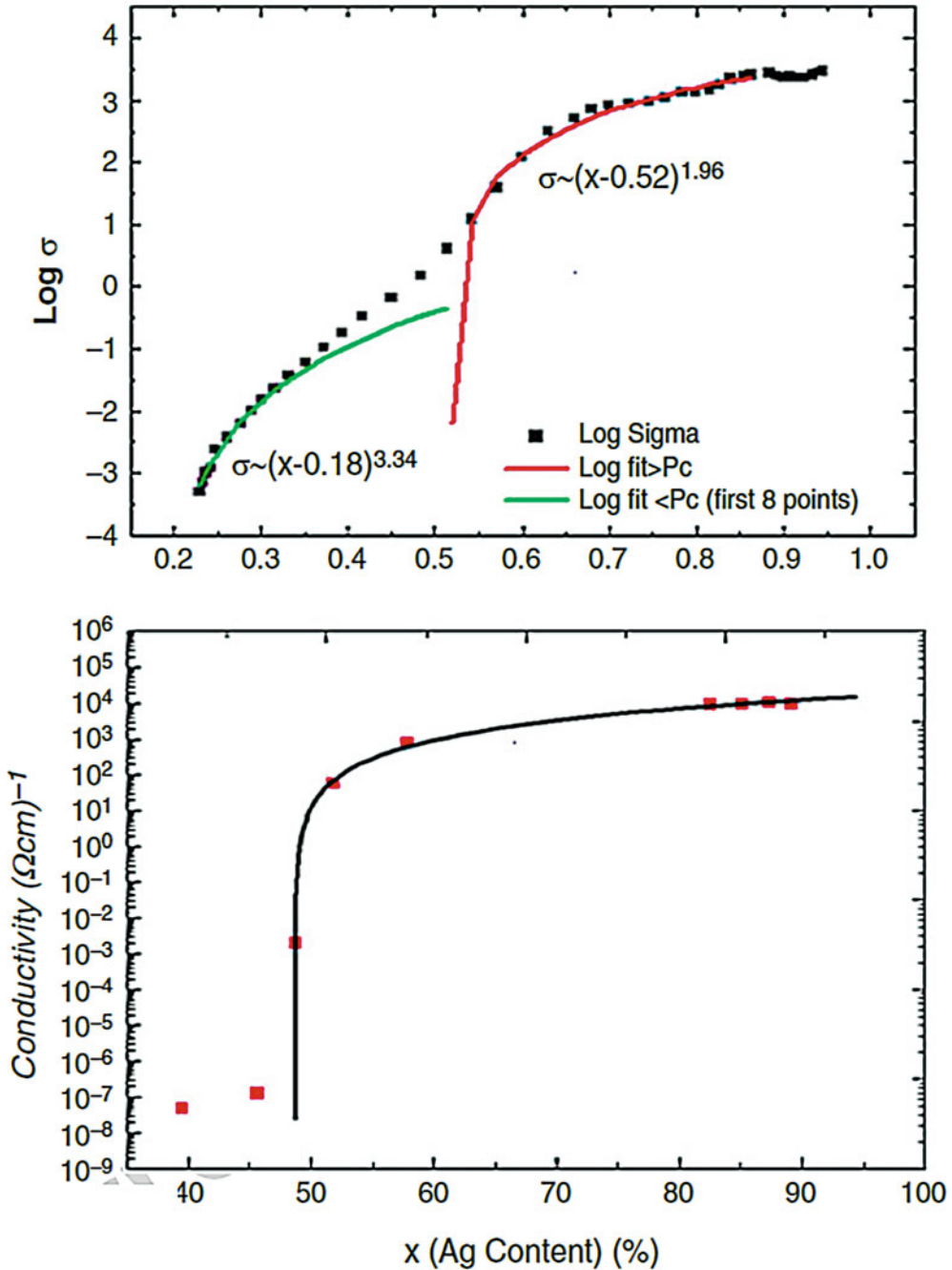
Following this finding, it is apparent that the lower conductivity stair in the upper panel has to do with tunneling between nearest-neighbor isolated particles. This is further confirmed by the $t > t_{\text{un}}$ nonuniversal dependence of that lower stair. The fact that there is an apparent percolation threshold for that stair indicates that there is a limited range where the tunneling is still effective to make the conductivity associated with it observable. To further substantiate all that and to show that there is an analogy with the staircase in the lattice, that is, having a radial distribution function with peaks, let us consider the conductivity of the same composite as in Fig. 16 but prior to the annealing, that is, where the grains at the lower x values did not coalesce. In the upper panel of Fig. 17 we see then three stairs with well-defined thresholds and a slightly nonuniversal exponent. This nonuniversal behavior in the tunneling case is associated with the distribution of the distances from a given particle to its neighbors. If those are, as in lattices, at well-defined discrete distances, one will get the universal behavior throughout the stair, while if there is, say, a Gaussian distribution of distances to a given neighbor, the far tail of the distribution will result in the conditions for the nonuniversal behavior. To appreciate this conclusion one recalls that for the i th neighbor, σ_{i0} of Eq. (52), is simply given by the constant $\sigma_{i0} \propto \exp(2l_i/d)$ while in the case of a width to the l_i peak it will be given by $\sigma_{i0} \propto (p-p_c)^{a/(1-a)}$ dependence within the stair (see Eqs. (11) and (18)).

To further confirm the above interpretation and to show that there is, in an analogy with the lattice case, a radial distribution function (RDF) with peaks, we show in the upper panel of Fig. 17 the behavior of the same composite that was used in the lower panel of Fig. 16, but before the annealing (i.e., before the coalescence of grains). The presence of the RDF is illustrated by the inset that describes various rings of neighbors as suggested by the electron micrograph that was taken on such a composite, and is shown by the other inset in that figure. We see then in Fig. 17 stairs with well-developed three percolation thresholds. The upper two have slightly off universal exponents while the lowest one exhibits a

high nonuniversal exponent. The reason for the first two is the width of the peaks in the RDF that are shown for the nearest and second nearest neighbors, while for farther neighbors, the RDF becomes continuous-like and this results in a large value exponent (see e.g., Eq. (47)).

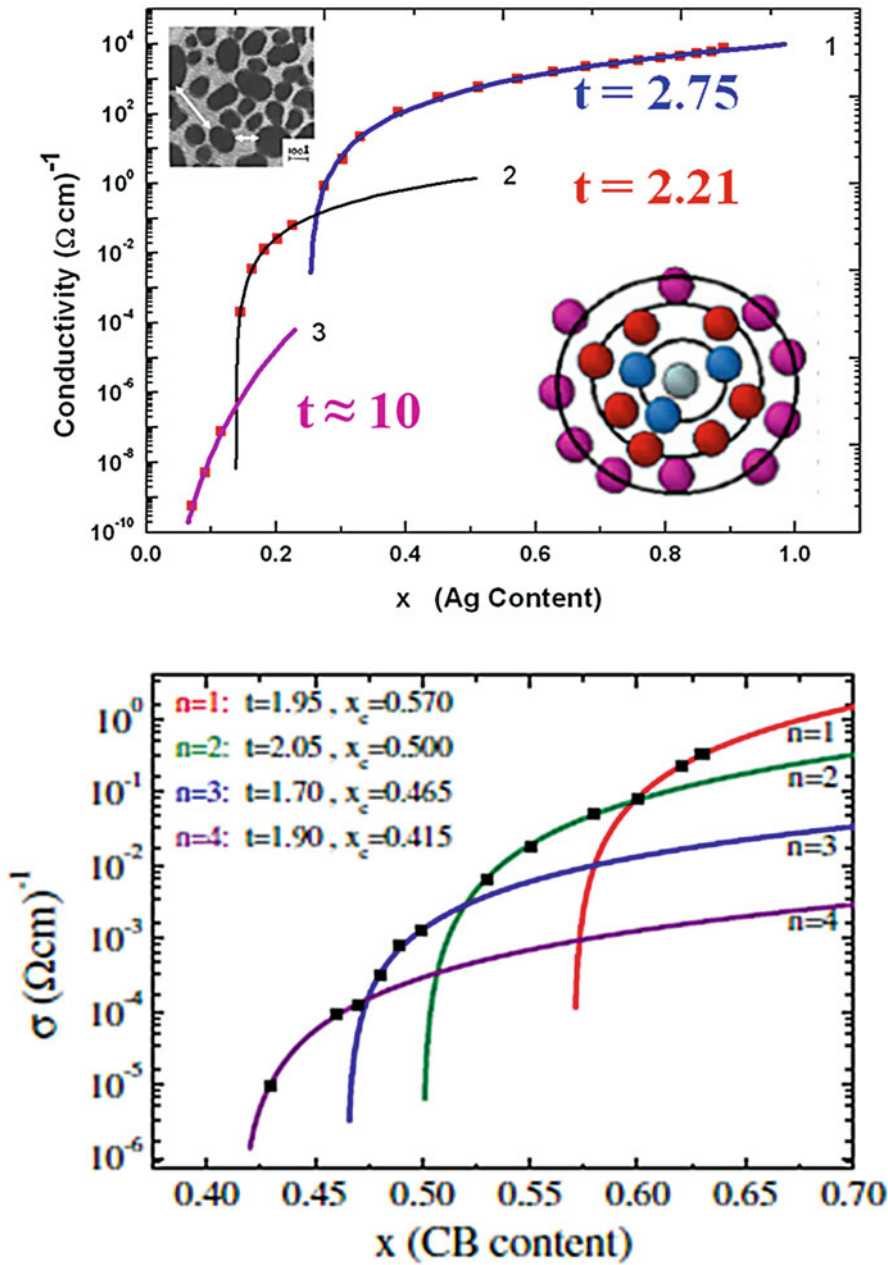
Comparing the results on granular metals with the corresponding results on carbon black (CB) polymer composite that consists of sphere-like particles reveals a staircase behavior but all the exponents are universal. The difference between the behaviors of the two types of systems can be well understood (Toker et al. 2003) by considering the fact that the radius of the carbon black particles $R(\text{CB})$ is an order of magnitude larger than the tunneling range d as well as the size of the metallic grains, $R(\text{GM})$. Hence, only near neighbors tunneling is possible in the CB case (see Fig. 15). The system in the latter case consists then of spheres between which there is a tunneling barrier, such that the resistance associated with the second stair is a sum of the two subsequent resistors where each of them is associated with the tunneling between nearest neighbor particles. This picture is well supported by the finding that the polymer actually provides a constant thickness coating layer to the CB particles (Picu and Rakshit 2007). The amplitude of each stair represents then the probability that a corresponding path of consecutive nearest neighbors will exist. This (in some analogy to the Bethe lattice (Stauffer and Aharony 1992)) explains both the higher density of the $x_{c,i}$ s and the smaller conductivity jumps in comparison with those encountered in the granular metals (Balberg et al. 2013). The microscopic physical difference between those two types of composites is conveyed by Fig. 15, which was derived following a detailed conductance atomic force spectroscopy, on those two systems (Toker et al. 2003).

In summary, the tunneling contribution of the first upper stairs in Fig. 17, with a slight deviation from universality in the granular metal, is due to the widened peak in the radial distribution of the grains' distances, and then, for the lowest stair, the continuous distribution of farther neighbor distances leads to the observation of very high nonuniversal exponent. On the other hand, in the



Principles of the Theory of Continuum Percolation, Fig. 16 typical dependences of the conductivity on the metallic volume content in granular metals (in the upper panel Ni–SiO₂, in the lower panel Ag–Al₂O₃ after annealing at 600 K). In both cases there is a typical x_c threshold of 50 vol.% and a universal behavior of $t \approx t_{un}$ in the $x > x_c$ regime. This behavior is clearly associated with

the presence of a continuous metallic network. The conductivity dependence for $x < x_c$ in the upper panel confirms the presence of a tunneling transport between isolated grains prior to the onset of that network. The $t > t_{un}$ observation there confirms the nonuniversal behavior that was considered above. (From Balberg (2009a) and Balberg et al. (2015))



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Fig. 17 The confirmation of the percolation staircase model due to tunneling in non-annealed Ag–Al₂O₃ granular metal (GM), in the upper panel, and in (N990) carbon black-polymer composite (where the carbon black particles are nearly spherical) in the lower panel. In the insets one sees a typical electron micrograph of a granular metal

(38 vol.%) below the percolation full coalescence threshold (50 vol.%, see Fig. 16) and the corresponding tunneling rings model that is applied in order to account for the staircase behavior. In the lower panel we show the staircase that is obtained for a composite of spherical carbon black particles that are embedded in a polymer. (From Balberg et al. (2013) and Ravid (2012))

carbon black composite behavior that is shown in the lower panel of Fig. 17, the particles size is more than an order of magnitude larger than the tunneling distance. Hence, the resistors that contribute to the conductivity in the system are only those of the tunneling between nearest neighbor where the inter-neighbor resistance is determined by the polymer layer that encapsulate the particles. Correspondingly, each n , in the lower panel of Fig. 17, presents the n th ($n \geq 1$) favorable conduction path in the system. The conductivity ratio represents then mainly the number of tunneling “junctions” in the path but also the fewer such paths available. This model is supported by the smaller jumps and the smaller x_c stairs-intervals in comparison with the case of the granular metals.

Finally, we note that other kinds of staircases can be found. For example, Hu et al. (2008) found abrupt conductivity stairs due to percolation onsets between aggregates that are composed of the conducting particles themselves. This phenomenon has shown up by a $\perp$ shape stairs where the increase of x (or N) does not actually change the concentration of the inter-aggregate channels and thus within a given stair there is hardly a conductivity dependence on x . In a way, the latter process is reminiscent of adding individual electrons to a metal sphere. Such a phenomenon may also explain the results of Mukherjee et al. (2014) on some metal-semiconductor nanocomposites.

Further Extensions for Various Off-Universal Conductivity Exponents in Continuum Systems

The Range of Pseudononuniversal Exponents in Continuum Systems

In many systems in the continuum nonuniversal like, $t > t_{un}$, exponents have been observed despite the fact that they are not associated with the divergence of the conductance value distribution that we have described in sections “The Percolation Behavior of the Electrical Conductivity” and “Universal and Non Universal Behaviors of the Electrical Conductivity.” We call this new class of exponents the pseudononuniversal exponents (Balberg 2017). For the explanation of that,

a priori, unexpected phenomenon, let us consider percolation systems where the critical phase transition-like behavior does not apply, that is, when, say, p_s in a lattice deviates considerably from p_{sc} . This regime (as in Eq. (20)) is known as the effective medium regime, which differs from the so-called critical regime where the phase transition behavior (that was described in sections “The Critical Behavior of Percolation Clusters” and “The Critical Behavior in the Continuum”) is practically maintained. As there are excellent reviews of the theory of the effective medium regime (Kirkpatrick 1973; Sahimi 2003; Nan 1993) we give here only a brief introduction to this topic that appears to be sufficient for our discussion of the pseudononuniversal exponents.

The above Eqs. (9) and (10) of the phase-transition behavior of percolation theory of the electrical conductivity were determined by the classical asymptotic-scaling principle of percolation theory (see section “The Historical Bridge Between Lattice and Continuum Percolation” (Shklovskii and Efros 1984; Stauffer and Aharony 1992; Bunde and Havlin 1991)). That behavior takes place at the dilute (low occupation) but still connected (or “percolating”) limit of that system. However, as p_b (or p_s) departs from p_{bc} (or p_{sc}), that is, when the system becomes denser, the conductivity is not expected to be well accounted for by those equations since the increase of p_b (in particular as $p_b \rightarrow 1$) does not significantly change the connectivity of the system. The behavior in the dense regime was quantitatively accounted for in the seminal work of Kirkpatrick (1973). His effective medium approximation (EMA) was based on the current continuity between an individual current-carrying element and the effective medium in which it is embedded. For the sake of finding the global electrical conductivity in this effective medium, the EMA considers some average local conductance value that can be assumed to be the same for all the “potentially” conducting elements including the non-occupied bonds in the lattice. This average is determined by the minimization (or nulling) of the sum of the current fluctuations in the electrical network (Sahimi 2003; Nan 1993; Clerc et al. 1990). Using that procedure, the dependence of

the conductivity on the percolation probability was found to be given by Eq. (20).

From the above short description it is apparent that the applicability of the percolation and EMA approaches depends on the deviation of p_b from p_{bc} , and thus, with the increase of this deviation there will be a continuous transition in the dependence of $\sigma(p_b)$ (Kirkpatrick 1973; Li and Strieder 1982; Mitescu et al. 1982), from that of the above percolation critical behavior of Eqs. (9) and (10) to that of the EMA (Eq. (20)) dependence. The important point here is that no suggestion was proposed for the particular behavior of the conductivity in the intermediate regime between the scaling and effective medium regimes, but it is widely accepted that there is simply a gradual-smooth transition between those two asymptotic regimes (Kirkpatrick 1973; Keblinski and Cleri 2004; Li and Strieder 1982; Lobb et al. 1981). In fact, the entire behavior between p_{sc} and $p_s = 1$ can be closely fitted by a single analytic expression (Li and Strieder 1982) and it was fitted (Lobb et al. 1981) by a $t(p_b - p_{bc})$ expression throughout the entire possible p_{bc} to $p_b = 1$ range. The only differences between the various works is the value of p_b (or p_s) from which the EMA dominates the behavior and how gradual is the transition between the above two asymptotic behaviors. These differences depend on the lattice structure as well as on the method that was used for the determination of the $\sigma(p_s - p_{sc})$ or the $\sigma(p_b - p_{bc})$ dependencies. In passing we recall that the common parameter that is meaningful and helpful for a quantitative characterization of the deviation of p_s from p_{sc} (or p_b from p_{bc}) is the normalized quantity $p_d = (p_s - p_{sc})/p_{sc}$ (Keblinski and Cleri 2004) (or $(p_b - p_{bc})/p_{bc}$ (Balberg 2017)). The abovementioned transition between the scaling (or critical) and the effective medium behaviors is manifested then by the variation of the conductivity exponent, t , from $\mu \equiv t_{un}$ to $v \equiv 1$, as well as, by the change of the *extrapolated threshold* from p_{bc} to p_{bec} (see Eq. (20)). This transition, of the value of t with the increase of p_b , was predicted theoretically (Nan 1993; Lobb et al. 1981) and observed numerically by many computer simulations (Kirkpatrick 1973; Keblinski and Cleri 2004; Li and Strieder 1982).

Turning to the $t > t_{un}$ phenomenon with which we are concerned here, let us consider a 2D system of randomly implanted line segment (or “sticks”) (Balberg et al. 1991; Li and Zhang 2010; Zvezelj and Stankovic 2012) such as those frequently used to represent CNT composites (Keblinski and Cleri 2004; Balberg 2012; Mutiso and Winey 2013). In the sticks systems, as illustrated in the inset of Fig. 12, one has a concentration of n_{st} sticks and there are, say, on the average, m intersections per stick. Doubling n_{st} also doubles m and thus the total concentration of the intersections (hereafter the junctions) n_j , will quadruple with n_{st} , that is, $n_j \propto n_{st}^2$. This simple intuitive conclusion (Mutiso and Winey 2013) that has been confirmed by the simulations of Zvezelj and Stankovic (2012) is reminiscent of the $p_b = p_s^2$ relation (Eq. (1)) that we mentioned for lattices. Thus, one can establish now the $p_s \leftrightarrow n_{st}$ and $p_b \leftrightarrow n_j$ analogs of the two systems. Letting n_{stc} be the threshold for the onset of conductivity yields that $n_{std} \equiv (n_{st} - n_{stc})/n_{stc}$ is then the analog of p_d and x_d that we mentioned in sections “The Percolation Behavior of the Electrical Conductivity” and “Universal and Non Universal Behaviors of the Electrical Conductivity.” However, unlike lattices and lattice-like systems (as in Fig. 1) where p_s and p_b have confined values, for permeable-like sticks (see (Balberg 2012) and the inset in Fig. 12)) there is, in practice, no limit to n_{st} (Keblinski and Cleri 2004; Zvezelj and Stankovic 2012). Following that and the above analogy, let us start by assigning a resistance of the order R_{st} to each stick and a resistance of the order of R_j to each intersection. For $R_{st} \gg R_j$, we have, as expected intuitively, that the sticks are both the *geometrical bonds* and the electrical bonds of the system (Balberg et al. 1991), while the intersections are the geometrical sites and the electrical junctions of the system. Hence, we expect (Andrade et al. 2000), as in Eqs. (8), (9), and (10), the classical dependence of $\sigma \propto (1/R_{st})(n_{st} - n_{stc})^\mu$. On the other hand if $R_j \gg R_{st}$ the dominant electrical bonds in the system are the intersection-junctions, as in the site percolation problem (Yuge 1977) and as in the common interparticle tunneling in many composites (Bauhofer and Kovacs 2009). Hence, due to

universality (see section “The Percolation Behavior of the Electrical Conductivity”), the conductivity is also given, by $\sigma \propto (1/R_j)(n_j - n_{jc})^\mu$, where μ is the universal critical exponent t_{un} (see Eq. (10)) and n_{jc} is the corresponding conductivity threshold. Considering the above $n_j \propto n_{st}^2$ relation, the above analog, and the fact that n_{st} is, in practice, the only available known (or “controllable”) parameter, we have that

$$\begin{aligned} \sigma &\propto (1/R_j)(n_j - n_{jc})^\mu \\ &\propto (1/R_j)(n_{st}^2 - n_{stc}^2)^\mu. \end{aligned} \quad (53)$$

What Eq. (53) tells us is that in addition to the $t_{un} \rightarrow 1$ transition (from the scaling to the EMA behavior that is expected for the $R_{st} \gg R_j$ case with the increase of n_{st}), for the combined case of $R_j \gg R_{st}$ (Eq. (53)) and $n_d \equiv (n_{st} - n_{stc})/n_{stc} \gg 1$, we also expect an exponent transition from μ to 2μ , to 2 and to 1. Of course, depending on the system, the expected observation will exhibit the entire, or a part of this series of exponents (Balberg 2017). Indeed, simulations of the corresponding systems (Kebblinski and Cleri 2004; Li and Zhang 2010; Zezelj and Stankovic 2012; Mutiso and Winey 2013) have shown the fulfillment of the expected $t_{un} \rightarrow 1$ transition for the $R_{st} \gg R_j$ case and the increase of t with the increase of n_{st} beyond μ (Li and Zhang 2010; Zezelj and Stankovic 2012; Mutiso and Winey 2013) (even up to $t = 2\mu$ (Kang and Kim 2011)) for the $R_j \gg R_{st}$ case. Indeed, with the increase of the R_j/R_{st} ratio a continuous variation from that of the first case to that of the second case has been found by simulations in Li and Zhang (2010) and Zezelj and Stankovic (2012). This suggests that the same conclusions apply to carbon nanotube (CNT) and graphene-based composites (Balberg 2012).

The important point to note here is that in all those simulations no g -value distribution (Dalmás et al. 2006; Aharony 1980; Shante and Kirkpatrick 1971), no change in the systems’ dimensions, and no anisotropy (Rapp et al. 2005; Lobb et al. 1981) were introduced, and thus, the $t > \mu$ results cannot be attributed to either of those “classical” non-universal effects. In fact it appears that the majority of the observed $t > \mu$ values in the continuum, up to

and including $2\mu = 2.6$ (in 2D) and $2\mu = 4.0$ (in 3D) values are due to the above $R_j \gg R_{st}$ effect. The latter conjecture is proven by the fact that the statistics of all the above experimental (Sahimi 2003; Bauhofer and Kovacs 2009) and computational (Kebblinski and Cleri 2004; Li and Zhang 2010; Zezelj and Stankovic 2012; Mutiso and Winey 2013; Kang and Kim 2011) data exhibit the confinement of the t values to the $\mu \leq t \leq 2\mu$ range. Moreover, there is already available experimental evidence (Combessis et al. 2013) for our prediction that the smaller the threshold the more likely the observation of this effect due to the lower $x_d \propto n_d$. The fact that the same confinement of the t values applies both, to composite materials (Bauhofer and Kovacs 2009) and to porous media (Sahimi 2003) provides then a firm support to the above site-bond like model for the pseudo-nonuniversal t values in many continuum systems.

Possible $t < t_{un}$ Values in Some Composite Materials

From all the above we got used to t values that are larger than the universal values. There are, however, also many experimental (Bauhofer and Kovacs 2009; Eda et al. 2009; Fan et al. 2010; Pang et al. 2010; Mukherjee et al. 2014; Shao et al. 2008; Pang et al. 2013) and computational (Rahatekar 2005; Grujicic et al. 2004) reports for continuum systems for which t is smaller than the relevant universal μ (Zezelj and Stankovic 2012; Derrida et al. 1984) and even smaller than $t = 1$ value (i.e., smaller than expected from the EMA, see Eq. (20) and (Kirkpatrick 1973; Sahimi 2003; Nan 1993)). In particular, experimental values of $t = 1.2$ for CNT composites (Sandler 2003) and as low as a $t = 0.4$ value for segregated composites were found (Mukherjee et al. 2014; Shao et al. 2008; Pang et al. 2013). Such low values are not consistent with the abovementioned universal values (even if one assumes (Mitchell and Krishnamoorti 2007) a 2D conducting sub-network within the 3D system). These $t < \mu$ observations are quite surprising in particular since they appear, a priori, to contradict the sound and well-established electrical conductivity as given by the simple links nodes blobs (LNB) model (Shklovskii and Efros 1984; Stauffer and Aharony 1992;

Bonde and Havlin 1991). This model, which was described in section “The Percolation Behavior of the Electrical Conductivity”, is the only widely accepted topological presentation of an electrical (Kirchhoff’s laws obeying) percolation network from which the μ values were derived (see Fig. 3). The intriguing questions that arise then are whether the observed $t < \mu$ relations involve some other special universality class (as was suggested for other cases and different systems (Trugman and Weinrib 1985)), or if not, how can they be explained within the framework of the known percolation universality class (Stauffer and Aharony 1992; de Arcangelis et al. 1985)? To respond to this challenging puzzle within the framework of the universality class that we have considered throughout this review (see sections “The Critical Behavior of Percolation Clusters” and “The Critical Behavior in the Continuum”), let us apply the excluded volume considerations (Balberg et al. 1984a) (see section “The Percolation Threshold in the Continuum”) for systems such as CNT-polymer composites (Bauhofer and Kovacs 2009), for which $t < \mu$ values were reported. While we limit our analysis here to these composites we also suggest (see below) that the values of $t < \mu$, found in other systems (Eda et al. 2009; Fan et al. 2010; Pang et al. 2010; Mukherjee et al. 2014), result from the same basic reasons that we propose here for the CNT composites.

Recalling that in a system of permeable objects $B = nV_{\text{ex}}$ (see Eq. (24)) and following the corresponding percolation relations for lattices Eqs. (8), (9), and (10) and for the continuum (Eq. (37)) we have that:

$$\sigma \propto (B - B_c)^\mu \propto [(n - n_c)V_{\text{ex}}]^\mu, \quad (54)$$

where n is the concentration of the permeable objects and n_c its corresponding threshold. If $v \ll V_{\text{ex}}$ the connected system can be looked upon as a very dilute one (with total objects volume $nv \ll 1$), so that the total volume “covered” by the permeable particles, ϕ , can be a good approximation for the nonoverlapping permeable objects, that is, nV . This is since the volume of the particles’ “would be” intersections is negligible; being much smaller than nv , see Fig. 10. This is

very helpful for the present consideration of the nonpermeable CNTs since nV is then also the (trivial) general expression for the fractional volume, x , of the nonpermeable (hard-core) particles (see Eqs. (33) and (34)). Hence, in systems with $x \ll 1$ values, such as CNT (Bauhofer and Kovacs 2009; Du et al. 2005; Kim et al. 2005) or graphene (Eda et al. 2009; Fan et al. 2010; Pang et al. 2010) composites, we can use the results obtained for permeable particles (Balberg 2012), yielding that in Eq. (54) we can write, as in Eq. (33), that $B \approx xV_{\text{ex}}/v$. Now, we know that for long cylinders of length L and radius r (representing CNTs (Ahmad et al. 2006)) $v = \pi r^2 L$ and, for $L \gg r$, $V_{\text{ex}} = 4rL^2 \langle \sin\theta \rangle$ (see section “The Percolation Threshold in the Continuum” and Eq. (25)), where $\langle \sin\theta \rangle$ is an average over the relative orientations of CNT pairs (Balberg et al. 1984a; Kim et al. 2005). Substituting these expressions for v and V_{ex} in B we get that

$$B = (4/\pi)(xL/r) \langle \sin\theta \rangle. \quad (55)$$

Here we note that, typically, the maximum of the B values that are topologically involved in percolation studies is smaller than 10 (Balberg and Binenbaum 1987b; Balberg 1985; Shao et al. 2008). From this and the value of $B_c \approx 2$ (see Eqs. (26) and (33)) it follows that the very large $V_{\text{ex}}/v = (4/\pi)(L/r) \langle \sin\theta \rangle$ values will yield very small x values (and thus also the very small ($\ll 1$) percolation threshold values of x_c^0 in CNT-polymer composites (Ahmad et al. 2006).

Following Eq. (55) let us examine now the possible effects of the variations of the systems’ parameters L , r , and $\langle \sin\theta \rangle$ with x , on the dependence of B on x (Janzen 1975; Celzard 1996). First, the increase of x can result in the increase of flocculation (Pang et al. 2010; Tunncliffe et al. 2014; Meier et al. 2007; Wu et al. 2000), that is, the “breaking” of the particles that makes the average L to decrease with x due to direct or indirect “friction” between the particles (Tunncliffe et al. 2014). On the other hand, the increase of x can lead to particles bundling (Ounaies et al. 2003; Bao et al. 2013; Kymakis and Amaratunga 2006), that is, to the increases of

r with x . Also, in some molding processes the alignment of (especially elongated) particles can lead to the decrease of $\langle \sin\theta \rangle$ with x (Du et al. 2005; Eken et al. 2011; Sandler et al. 2003; Abbasi et al. 2010; Goh et al. 2019) (see also Fig. 9 and Foygell et al. (2001) and Balberg et al. (2016)). Hence, considering these dependencies we have that B in Eq. (55) is given by the resulting function $B(x) \propto x[L(x) \langle \sin\theta \rangle(x)]/r(x)$. In addition, considering the possible variation of the percolation threshold due to the above processes, we denote now the value of x that is associated with $B_c = n_c V_{ex}$ in Eq. (54), by x_c . This x_c is expected to be different than x_c^0 that follows the standard experimental or computational analysis where the values of L , r , and $\langle \sin\theta \rangle$ are independent of x (as in many conductor/insulator two-phase continuum systems (Hunt and Ewing 2009; Zallen 1983; Sahimi 2003; Balberg 2009a)) and is given by

$$\sigma = \sigma_0 (x - x_c^0)^t. \quad (56)$$

In those standard analyses σ_0 , x_c^0 , and t are determined by the fit of the $\sigma(x)$ data that is found experimentally or computationally to Eq. (56). We expect then that for every reasonable (in the above context of CNT composites) x -decreasing $B(x)/x \propto [L(x) \langle \sin\theta \rangle(x)]/r(x)$ function of Eq. (55), the corresponding conductivity exponent will vary with x . To see if and how such dependences can lead to a $t < \mu$ behavior we examine below a couple of such $B(x)$ dependences. We remark here in passing that in general the molding processes do not necessarily yield that $t < \mu$ (e.g., due to presence of effects such as the above described divergence of $\langle g \rangle$ (see sections “The Percolation Behavior of the Electrical Conductivity” and “Universal and Non Universal Behaviors of the Electrical Conductivity”), which can lead in the opposite direction, that is, to $t > \mu$ values.

For a transparent and simple illustration of the $t < \mu$ puzzle and its solution let us assume that in the x region of interest (i.e., $x > x_c$) the effect of x on L due to flocculation can be described (phenomenologically) by $L = L_0(x/x_c)^{-\beta_1}$, where L_0 is the value of the average L at the percolation threshold x_c . Similarly we can use $r \propto (x/x_c)^{\beta_2}$ and $\langle \sin\theta \rangle \propto (x/x_c)^{-\beta_3}$, where for each of these

effects (that take place during the fabrication of the composite) a different value of $\beta_i > 0$ may apply. We get then that for this simple model the combined effect of all these processes may yield that $B(x) \propto xL \langle \sin\theta \rangle / r \propto x^\Gamma$ where $\Gamma = 1 - (\beta_1 + \beta_2 + \beta_3)$. One notes of course that since the functional dependence of the system parameters on x , following its processing, is not available explicitly at present (experimentally or theoretically), our above model is just a possible illustrative description of how the x -decreasing $B(x)/x$ dependence can result in the $t < \mu$ observation. Considering the dependence of B on x^Γ and Eqs. (54) and (55) we get that:

$$\sigma = A(x^\Gamma - x_c^\Gamma)^\mu, \quad (57)$$

where A is an x -independent constant. Since σ is found always (experimentally or computationally) to increase with x , one concludes from Eq. (57) that $\Gamma > 0$. For the extreme case where B deviates enough from B_c the conductivity exponent t approaches $\Gamma\mu$. The condition that $B(x)/x$ will be then a decreasing function of x , that will yield in this model that $t < \mu$, requires that $\Gamma < 1$.

Assuming that Eq. (57) describes the real behavior of some systems, we suggest that in the many experimental (Shao et al. 2008; Pang et al. 2013) and computational (Rahatekar 2005; Grujicic et al. 2004) works that showed the $t < \mu$ effect, the analysis that was performed was to fit the classical Eq. (56)-like behavior by using data that is actually given by an Eq. (57)-like dependence. Indeed, as described in Balberg et al. (2016) a numerical justification for that interpretation was obtained by fitting data that was produced by using Eq. (57) to the dependence given by Eq. (56). However, for brevity and clarity let us provide an analytic proof for this interpretation. For this purpose, let us distinguish between two extreme cases. In the first case we consider the fitting to Eq. (56) in an x interval for which $x^\Gamma \gg x_c^\Gamma$ and $x \gg x_c^0$. In this case, one actually fits the data to a $\sigma \propto x^t$ dependence. However, according to Eq. (57) $\sigma \propto x^{\Gamma\mu}$ which yields that $t = \Gamma\mu$ and then, since $\Gamma < 1$, a $t < \mu$ value, is found. The second case is the other extreme where the examined x -range is close to x_c^0 . Equating

Eqs. (56) and (57)) one gets then that $x^{\Gamma-x_c^0} = (\sigma_0/A)^{1/\mu}(x-x_c^0)^{t/\mu}$. The derivatives of both sides of the equation have to be the same and thus $\Gamma x^{\Gamma-1} = (\sigma_0/A)^{1/\mu}(t/\mu)(x-x_c^0)^{(t/\mu)-1}$. However, for $x \rightarrow x_c^0$ the derivative on the left hand side of this equation has a finite (> 0) value, for any x , while the derivative on the right hand side of it (for $x-x_c^0 \rightarrow 0$) will have a finite value only for $t = \mu$. Hence, the value of t will vary from $\Gamma\mu$, when $x \gg x_c^0$, to $t = \mu$ as x approaches x_c^0 . Indeed, taking $\mu = 2$ in the numerical justification (Balberg et al. 2016), t values between $t = 1.4$ and $t = 0.6$ were derived, by applying Eq. (56).

To show that our choice of the above particular x^β dependence is not a necessary condition or a unique example for obtaining the $t < \mu$ behavior, we have also substituted the phenomenological $B(x) \propto xL(x) \propto x/(1+x^2)$ dependence (with $\mu = 2$ and $x_c = 0.1$) in Eq. (54). This yielded, as in the above case, to the decrease of the value of t from $t = 2$ to $t = 0.88$ with the increase of x above x_c (Balberg et al. 2016). We thus conclude that in the continuum, there are systems where B can have a sublinear dependence on the particle concentration that brings about to the observation of a “measured” or simulated $t < \mu$ values. Those values are associated with the variation of the character of the system with the change of x . Similar conclusions, considering the term $\langle \sin\theta \rangle$ were shown (Balberg et al. 2016) to be applicable to the increase of the alignment (Bao et al. 2013; Kymakis and Amaratunga 2006; Eken et al. 2011; Sandler et al. 2003; Abbasi et al. 2010; Goh et al. 2019) that was found in CNT-polymer composites.

The physics of the above-derived behavior is quite simple; while the exponent μ represents the changes in the (phase transition like) connectivity that determines the critical behavior, the exponent Γ accounts for the x -dependent changes in the basic parameters of the system (here, L , r , and $\langle \sin\theta \rangle$). In particular, if x is very close to x_c^0 the character of the system due to flocculation (i.e., the average value of L and thus the corresponding value of n) has not been changed significantly compared to that at x_c^0 . In contrast, when x and x_c^0 are far apart, the system’s character (e.g., the decrease of L and the corresponding

increase of n with the increase of x) could have varied considerably. Hence, universality will always dominate when $x \rightarrow x_c^0$, but as x departs from x_c^0 a $t < \mu$ value may be exhibited by the “measured exponent.” As preliminary recent experimental evidence for this behavior, we can consider the results of Grunlan et al. (2001) and of Mukherjee et al. (2014) on segregated composites for which they found that with the departure of the x intervals from x_c^0 , the t values decreased from 1.87 to 0.90 and from 0.8 to 0.4, respectively. Note that these values were derived from experimental results on macroscopic systems and thus, there are no finite size effects, or deviations from percolation criticality, that may drive the conductivity exponent below $t = 1$.

Hopping in Percolation Systems

While the correlation between percolation and hopping conductivity was suggested a long time ago (Shklovskii and Efros 1984; Kirkpatrick 1973; Adler et al. 1973) there was no direct experimental confirmation of it. In particular, no experimental proven relation between the concentration of the conducting elements and the temperature dependence of the conductivity has been reported. It turns out that while corresponding data was available, it was only recently that those were put in a framework that enabled to demonstrate explicitly that this relation is also suggested by experimental data. As shown below this framework is that of the nonuniversal behavior that we discussed in sections “The Percolation Behavior of the Electrical Conductivity” and “Universal and Non Universal Behaviors of the Electrical Conductivity” (Balberg and Jedrzejewski 2015).

In variable range hopping (VRH), in contrast with the simple tunneling-percolation models, one considers also the constraint of the energy needed in order to enable the excitation from an occupied to an unoccupied state (Shklovskii and Efros 1984) such as between two metallic spheres in a composite (Toker et al. 2003). This yields an optimal tunneling range, R_h , that is determined by the wave function (or electron localization) decay length, d , and the thermal excitation. The distance R_h is then the characteristic length of the effective local conductance in the macroscopic

network of the electrical conductivity in the system. In the studies of VRH in general (Shklovskii and Efros 1984), and their relevance to granular metal composites (GMCs) (Abeles 1976) in particular, the information on the VRH (Shklovskii and Efros 1984; Zabet-Khosousi and Dhirani 2008) was derived from the dependencies of the electrical conductivity σ on the temperature, T , or the applied electric field, F (Zabet-Khosousi and Dhirani 2008; Dugay et al. 2014; Simanek 1981; Entin-Wohlman et al. 1983; Adkins 1989; Zvyagin and Keiper 2001). However, there is rarely an additional or a more direct experimental evidence, to support the VRH models for such composites. In particular, the basic parameter R_h has been derived only indirectly from those dependencies (Zabet-Khosousi and Dhirani 2008; Dugay et al. 2014). This is quite of importance since the main objection (Zabet-Khosousi and Dhirani 2008; Simanek 1981; Entin-Wohlman et al. 1983; Adkins 1989) to the VRH interpretation of the behavior of the GMCs was that “the estimated hop distance appeared to be too small (of the order of the grain diameter or smaller) for VRH to be effective” (Zvyagin and Keiper 2001). In recent years, models, based on the presence of virtual states in the grains, have been proposed to account for this difficulty. In those models the “charges may bypass the Coulomb blockade barrier” following “two concurrent events, tunneling of an electron into a grain and the simultaneous escape of another electron from the same grain” (Zabet-Khosousi and Dhirani 2008). The major prediction of these models vis-à-vis the abovementioned objection was that R_h can be larger than the (nearly spherical) metal grain diameter $2b$. Hence, the primary test for an experimental verification of those “cotunneling” models (Zabet-Khosousi and Dhirani 2008; Dugay et al. 2014; Zvyagin and Keiper 2001) is the observation of $R_h > 2b$. While progress was made in confirming the latter models for arrays of ligand capped metal grains (Zabet-Khosousi and Dhirani 2008; Dugay et al. 2014), no corresponding advances, that is, evidence for $R_h > 2b$, were presented thus far for the GMCs which were the first arena of the above mentioned debate (Simanek 1981; Entin-Wohlman et al. 1983; Adkins 1989; Zvyagin and Keiper 2001).

Here we show that the parameter R_h in some GMCs can be derived from experimental results in a much more direct manner than from the simple $\sigma(T)$ or $\sigma(F)$ dependencies. This is by using temperature-dependent $\sigma(x)$ data, where x is the fractional volume content of the metallic phase (that is assumed to be proportional to the grain concentration) in the composite. Our approach is based on finding the local conductance transport-related length scale, ℓ , in systems where VRH is expected to exist, by mapping the VRH problem onto the predictions of the non-universal percolation theory (Kogut and Straley 1979) that we had applied previously (Balberg 1987a) for the “tunneling-percolation” (or the VRH, $T \rightarrow \infty$) problem, and that is briefly reviewed here in section “Universal and Non Universal Behaviors of the Electrical Conductivity.” The advantage of that approach for the presently considered VRH is that it separates between the large scale of the conducting network ξ (Balberg and Jędrzejewski 2015), that is, the percolation correlation length (Shklovskii and Efros 1984; Stauffer and Aharony 1992), and the small scale associated with the local effective conductances of which the network consists, ℓ . The quantity ℓ , in the $T \rightarrow \infty$ limit, is the $2(a-b)$ average of the near neighbor particle separation that we considered in section “Universal and Non Universal Behaviors of the Electrical Conductivity,” while in the VRH, the only local length scale is R_h . This suggests that $R_h/d \approx \ell/d$ so that we can obtain an estimate for R_h by such a mapping approach. We note, however, that there are two preconditions for the application of that approach to the conductivity data analysis in the context of VRH and composite systems. The first precondition is that the finger print of VRH, that is, the

$$\sigma(T) \propto \exp \left[-(T_0/T)^{1/2} \right], \quad (58)$$

dependence (Shklovskii and Efros 1984) (where the empirical parameter T_0 holds the information on the dominating transport mechanism (Abeles 1976; Entin-Wohlman et al. 1983; Adkins 1989)) is, as in Abeles et al. (1975a), convincingly exhibited by the data. The other precondition is

that the x values involved belong to the dielectric (i.e., the insulator-rich (Sheng 1992)) regime, for which one assumes that the observed macroscopic transport is dominated by tunneling between non-coalesced grains (Abeles 1976). This dielectric regime is well described by the x regime that lies below the onset of the coalescence related percolation behavior (see Fig. 16).

Dwelling somewhat on those preconditions we note that concerning the first, one can start from the classical VRH theories from which one expects that $\sigma(T) \propto \exp.(-2R_h/d)$ (Shklovskii and Efros 1984; Zabet-Khosousi and Dhirani 2008) and thus that $R_h/d \approx (T_0/T)^{1/2}$ (Entin-Wohlman et al. 1983; Adkins 1989). However, the answer to the question, whether such an R_h is just an effective system parameter, as T_0 , or an actual measurable length in the system, has not been given, thus far, in general, and for GMCs in particular. In what follows, we show that such a length scale is indeed present in a GMC in which the transport is dominated by VRH (i.e., where Eq. (58) is fulfilled). This finding will be shown then to suggest that the cotunneling process (Averin and Nazarov 1990; Feigleman and Ioselevich 2005; Beloborodov et al. 2005) applies at least to some GMCs. Hence, in view of the 40-year-old interest in the transport mechanism in the GMCs (Abeles 1976; Zabet-Khosousi and Dhirani 2008; Sheng 1992; Pollak and Atkins 1992), experimental evidence for the presence of such a process in them, that is of much theoretical (Adkins 1989; Beloborodov et al. 2005; Pollak and Atkins 1992) and practical (Kobayashi et al. 1998) interest, is called for.

Turning to the other precondition, we note that as the g 's that determine the system conductivity are those associated with the large interparticle distances (Balberg 1987a; Tyc and Halperin 1989), one can approximate the essence of the corresponding 3D (Poisson) distribution of those distances by the simplified mathematical expression of $h(r) \propto \exp.[-(r-2b)/\ell]$ where ℓ is a corresponding characteristic length of the interparticle distance (Balberg 1987a; Rubin et al. 1999) (see section “Universal and Non Universal Behaviors of the Electrical Conductivity”). For the interparticle tunneling conductance,

where $g \propto \exp.[-2(r-2b)/d]$, one obtains that for $d < \ell$ the local conductance distribution function, $f(g)$, can be given by $f(g) = (1-\alpha)g^{-\alpha}$ (Kogut and Straley 1979) where $\alpha = 1-(d/2\ell)$ (Balberg 1987a), and thus, that $\langle g^{-1} \rangle^{-1} \propto (x-x_c)^{(2\ell/d-1)}$. Hence, the superposition of the local conductance behavior, on the structural-geometrical behavior (see sections “The Percolation Behavior of the Electrical Conductivity” and “Universal and Non Universal Behaviors of the Electrical Conductivity”) takes then the form $\sigma(x) \propto \langle g^{-1} \rangle^{-1}(x-x_c)^t$ that can be written as:

$$\sigma(x) = \sigma_P(x - x_c)^t, \quad (59)$$

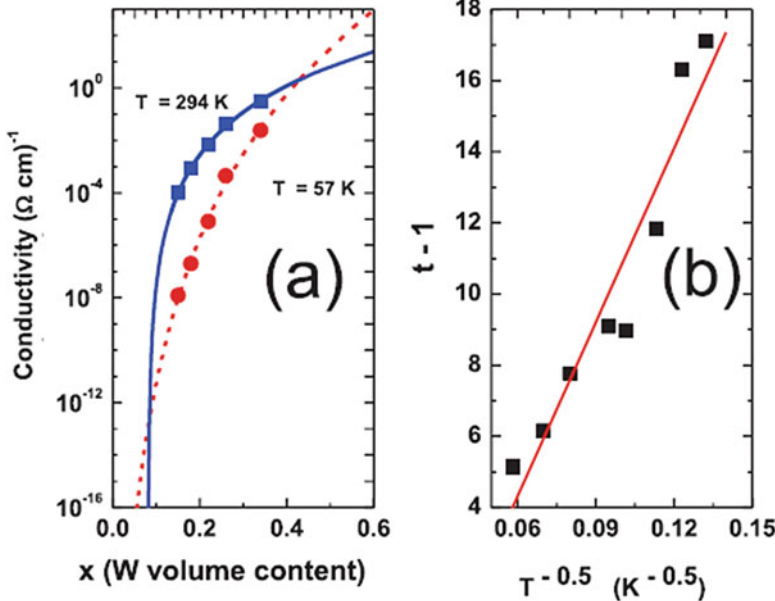
where σ_P is an x -independent parameter and $t = (t_{un}-1) + 2\ell/d$. In 3D, $t_{un} = \nu + \zeta \approx 2$ ($\nu = 0.85$ and $\zeta = 1.1$ (Stauffer and Aharony 1992; Zallen 1983)), and thus, $t-1 \approx 2\ell/d$ (Balberg 1987a). We note here that this result is based on the average of all the higher g , percolation-needed, conductances in the system (Balberg 1987a; Kogut and Straley 1979), but one can consider an average based on the one dimensional properties of the link (Hunt 1993) (see Fig. 2). The important observation for our purpose is that, following Eq. (59), we have a prediction for *a direct rigorous relation between the measurable quantity t and the ℓ/d ratio* which is between the mesoscopic and microscopic scales of the conduction elements in the system. Our assumption of a percolation behavior (Balberg 1987a), that is, that $\xi \gg \ell$, for the analysis of given experimental data will be justified if the critical behavior of Eq. (59) is fulfilled and if we can show that the value derived for ℓ can be associated with the local interparticle conduction mechanism. The length scale ξ shows that there is a “macroscopic” network that is determined by the connectivity of the system, while the other (say, the $\ell \propto 1/\sqrt{T}$) dependence, shows that ℓ can be related to a suggested mechanism. We note that the assumption $\xi \gg \ell$, applies for all the hopping mechanism mentioned above for granular metal systems. In the particular case of cotunneling, while providing the largest R_h , this length is only of the order of a few b 's (Zabet-Khosousi and Dhirani 2008; Beloborodov et al. 2005) which is

still a small segment of the correlation length ξ (or the link length in the LNB model (see section “The Percolation Behavior of the Electrical Conductivity”). In what follows we try to justify the above initial suggestion of the identification of R_h with ℓ in some GMCs.

As mentioned above, the common expectation of the VRH theories is that $R_h/d \propto 1/\sqrt{T}$. Hence, to support our conjecture that $\ell \approx R_h$ we have to show that the relation $t-1 = 2\ell/d \propto 1/\sqrt{T}$ is fulfilled by the results that we can extract from available data on GMCs. For getting the dependence of t on T , a series of temperature dependent $\sigma(x)$ data is needed. Examining the literature, we found, however, that $\sigma(x)$ data in various GMCs were given previously, either only for a couple of temperatures (Abeles 1976; Toker et al. 2003; Abeles et al. 1975b), or, that the data do not seem to fulfill the abovementioned preconditions for the verification of VRH in GMCs (Wey and Li 2013; Huth et al. 2009). On the other hand, we found that still to date, the most detailed and reliable $\sigma(T)$ data that

are compatible with Eq. (58), for a series of x values in GMCs, are those of Abeles et al. (Abeles 1976; Abeles et al. 1975a). This is in particular so for $W-Al_2O_3$ (Abeles et al. 1975a) in its dielectric regime, that is, in the above determined $0 \leq x \leq 0.34$ interval of the lower conductivity stair, as in the upper panels of Figs. 16 and 17. Following this realization we present those available $\sigma(T)$ data, for a series of x values, as $\sigma(x)$ results of the lower conductivity stair, for the series of the T values at which the conductivity was measured in Abeles et al. (1975a). From the latter results we derived the needed $t(T)$ values by fitting Eq. (59) to them (Balberg and Jędrzejewski 2015). In Fig. 18a we show then the $\sigma(x)$ dependence for two temperatures and in Fig. 18b we show the outcome of the procedure used, that is, the $1/\sqrt{T}$ dependence of the $t-1$ values, that were derived from those results.

From the latter results we see that the relation $t-1 = 2\ell/d \propto 1/\sqrt{T}$ is fulfilled, thus providing rather direct experimental evidence for the cotunneling



Principles of the Theory of Continuum Percolation, Fig. 18 (a) Typical T -dependent $\sigma(x)$ behaviors, as derived from the $\sigma(T)$ data for a series of x values, that were given in Fig. 4 of Abeles et al. (1975a). These x values belong to the dielectric regime (which constitutes the lower conductivity stair in the non-annealed $W-Al_2O_3$

granular metal composites that were studied). The curves in the figure present the best fits of Eq. (3) to the $\sigma(x)$ results for the two extreme temperatures of the eight that were studied there. (b) The $1/\sqrt{T}$ dependence of the $t-1$ values that were found from those fits. (From Balberg and Jędrzejewski 2015)

mechanism, on the one hand (Balberg and Jędrzejewski 2015), and showing the usefulness of the nonuniversal percolation behavior in providing quantitative information on a studied system, on the other hand. In particular, we show that conduction mechanism dependent distances that cannot be measured by structural-geometrical means can be determined by the application continuum percolation theory.

Future Directions

The relevance of the connectivity to the many areas of science, engineering, and technology as mentioned in the introduction makes the achievements in the theory of continuum percolation of great importance to the understanding and application of numerous natural and artificial systems. In particular, the understanding and conclusions derived from this theory in the last 40 years serve as guides to a scientific-based analysis of the various properties of many of those systems. Naturally then, future studies of continuum percolation are expected to proceed along two directions. The first is the further development of a rigorous basis for the theory itself and issues of principle such as the ones emphasized in the present review. The other direction is the application of the general conclusions and principles derived from the first development for the understanding of systems and properties such as those mentioned in regard to the electrical properties of percolation systems. The latter direction deserves quite a few extensions that will center on particular types of systems (say, solid composites and porous media) or particular properties (such as electrical noise, permeability of fluids, and elastic constants). Considering the wide scope of the corresponding many issues, we mention here, as examples, only a couple of them in particular those that are relevant to systems and properties that became of wide interest very recently. On the very basic-scientific level, a simpler rigorous establishment of continuum percolation as a phase transition is desired, in order to determine conclusively that the critical behavior of the geometrical-statistical properties are exactly the same as those of lattices.

Another fundamental theoretical problem is the derivation of the percolation and topological thresholds and critical exponents rigorously. A specific problem that needs attention in order to derive a more complete understanding of the percolation thresholds in continuum percolation is then the value of B_c at the hard-core limit. The first question that arises in that context is whether this can be done by another approach than the common one used thus far, that is, the application of the theory of liquids, and whether such an approach can yield better results than those of that application. The second question is whether, within the rather developed application of the theory of liquids, one can find a way to facilitate its implementation to the degree that will enable unbiased determination of percolation thresholds and critical exponents, as well as its utilization for “less trivial” objects than those considered thus far. On the more fundamental level of the latter problem, it is very interesting to know why is the above application so successful for the description of the percolation behavior, even though the theory of liquids was not designed for the study of phase transitions. Considering the empirical approach to the theory, we note that the usefulness and the generalization of the concept of “pointedness” have not been studied extensively in spite of its impressive predications concerning trends in the behavior of percolation thresholds in the continuum. The transparent physical-geometrical meaning of this concept calls then for its further utilization and quantification, on the one hand, and for trying to understand the reasons for its success, on the other hand. In particular, we note that at present, the latter concept can be used much more readily and for many more systems than the above mentioned rigorous approach that is based on the theory of liquids. Another question that has hardly been discussed in the literature is whether, in off-lattice systems, there will be an effect of the various disorders on percolation parameters other than the critical exponents, such as the critical amplitudes of the geometrical and/or the dynamical properties.

Turning to the behavior of the dynamical properties it appears that most of the basic principles of the corresponding theory are well understood by

now. However, the problem of variable “bond strengths” is not well accounted for, in general, and beyond the “strong-interaction” limit (e.g., tunneling only to nearest neighbors) in particular. The meaning of the percolation threshold in corresponding systems and the predictions of the corresponding critical behaviors are still an open question. In particular, the evaluation of the “residual” conductivity in comparison with that of the dominant percolation-like subnetwork has not been given thus far. For this, there is the need for the other corresponding parameters that characterize the charge, the mass, or energy transfer between the objects in the system. It further appears, however, that the most important information that one needs for the understanding of particular continuum systems, is the distribution function of the locations, the sizes, and the shapes of the objects in a system. As emphasized in this review, this information is usually scarce, thus limiting the possible applications of the general understanding and principles, outlined in our discussion regarding the critical behavior of the dynamical properties in the continuum, to specific systems. On the materials end, this includes cellular composites, and on the phenomenological end, this includes the various staircase-like behaviors. Here, the utilization of very modern experimental characterization techniques, such as local probe microscopies, should provide the link needed for that application. On the theoretical computational end, there is a need to derive the distribution functions associated with the structure, and thus with the dynamical physical properties in order to appreciate trends in the critical behavior (i.e., the values of the critical exponents) in various systems. These trends are expected to become amenable for examination with the improvement of the ability to produce or find systems where the percolation threshold can be approached much more closely than at present. This is both in the experiments and in the simulations. In the latter case, this is by considering much larger systems (in order to overcome finite size effects). Such developments are expected to yield the (generally missing so far) information on the dependence of the critical exponents on the proximity to the percolation threshold. This, as

well as the meaning of the percolation threshold when farther than closest neighbors are involved, such as in the tunneling-percolation case, are very much called for.

In order to illustrate the issues and systems whose understanding rests on the concepts mentioned above let us turn now to outline a few typical (of the many) questions associated with specific systems. Such are the effects of charging and quantum confinement of the corresponding particles that are embedded in a percolating system. The understanding of the interplay between these effects and the effects of the neighboring network is still in its infancy. This interplay has been shown recently to have a pronounce effect not only on the transport, but also on the photo-transport in such systems. Also, the effects of special features of the network, such as its fractal dimension, on the dynamical behavior are still a matter of controversy. Again, local probe microscopy, on the experimental end, and corresponding theoretical-computational work, on the other end, may resolve the corresponding problems. Another issue of great interest is the effect of the object’s shape beyond the convex objects that were dealt with in the present review. Such objects are found in composites and porous media that are of great present interest, for example, in systems where the objects can be described as having a “wavy” shape. A broader issue that is relevant to many systems, but for which no systematic discussion has been given thus far, is the relation between the trends in the critical behavior of the electrical, mechanical, and rheological properties, in corresponding solids or molten composites. These are of great importance in the fields of chemical-material and electrical-material engineering. Finally, a subject that has not been discussed in the context of continuum percolation, and, as we saw above, is mainly concerned with global properties of systems, is the statistics of finite clusters where there is, or there is no, interaction between the objects. This is of great importance for systems where the finite clusters determine the properties of interest, such as in cases where there is a charge transfer by a delocalization process.

Following the last part of this review, we conclude that attempts should be made to interpret

“strange” or “unexpected” values of the critical exponents that are observed experimentally, in light of the accepted fundamentals of the continuum percolation theory. Last but not least, trails should be made to utilize that theory in order to solve other problems in science in general, and for the derivation of otherwise non-measurable systems’ parameters (as in the hopping conduction problem) in particular.

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Bootstrap Percolation

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Glossary

Bethe lattice A graph of nodes (sites) each being linked to exactly z other nodes in the graph (z is the coordination number). The Bethe lattice is an infinite object such that there is no boundary and each node has an identical topology. Given any two nodes, there is only one unique set of links connecting them, so there are no closed loops. This is a regular graph with connectivity z . The Cayley tree, also a loopless graph with connectivity z , differs from the Bethe lattice in that a finite fraction of nodes leads to dead ends at a boundary (where they have connectivity 1).

Bootstrap percolation Also known as k -core percolation, is defined as follows. Given a collection of occupied (or active) and vacant (inactive) sites on a lattice, subsets might exist with the following property: Elements in each subset must be occupied and have at least k occupied neighbors, each of those occupied neighbor in turn belonging to the same subset. Bootstrap percolation occurs if any subset exists that spans the system from one end to the other.

Cluster Any subset of occupied sites, each having k or more occupied sites belonging to the same subset. The emergence of a spanning cluster underlies the bootstrap percolation transition.

Culling process Starting from an initial configuration, culling means that occupied sites with less than k neighbors are rendered vacant, i.e., “culled,” and the same operation is iterated a sufficient number of times as to achieve a final configuration with no more sites that are candidates for culling. The culling process is a practical protocol that leads to identify all the relevant subsets (i.e., clusters) in bootstrap percolation.

Lattice A collection of points (“sites”) generated from linear combinations with integral coefficients of some basis vectors. A d -dimensional lattice is generated from d basis vectors. Therefore, a d -dimensional lattice is a d -dimensional array or regularly spaced points. A lattice of finite size is such that all the integral coefficients have lower and upper bounds. The coordination number z is the number of sites (called the nearest neighbors) of equal least distance to any given site.

Random network A network (or graph) of nodes (sites) linked to other randomly chosen nodes. The network is characterized by the distribution of the degree (the number of neighbors of a node). We will discuss bootstrap percolation (or k -core percolation) on simple random, uncorrelated networks with arbitrary

degree distribution (we consider always undirected networks).

Regular lattice A regular lattice is a lattice generated from basis vectors that are Cartesian basis vectors, i.e., it is the set of points or a bounded proper subset of points in Z^d . A square lattice is the two-dimensional regular lattice whose basis vectors are $a(1,0)$ and $a(0,1)$; a simple cubic lattice has basis vectors $a(1,0,0)$, $a(0,1,0)$, and $a(0,0,1)$. A hypercubic lattice is a regular lattice of dimensionality $d > 3$. The coordination number z of a regular lattice equals $2d$. The length a is called the lattice spacing (it is set to unity here for practical purposes).

Definition of the Subject

In bootstrap percolation, we start with a lattice configuration of occupied and vacant sites. Occupied sites that have less than a certain prescribed number of occupied neighbors are rendered vacant, and as new occupied sites are found to satisfy the same condition, these are also rendered vacant. The process is iterated until eventually no more sites can be removed (if any exist). Bootstrap percolation endeavors to determine whether any occupied sites will survive the culling process and what the macroscopic geometrical properties of the occupied ensembles are. In essence, it is a generalization of conventional percolation which has led to many fruitful insights. A complementary view, which emphasizes the dynamical aspect of the bootstrap process, treats the vacant sites as invasive units and occupied sites as inert ones. Inert sites that are surrounded by too many invasive sites will become irreversibly infected and will start themselves to invade others. At the end, the question arises as to whether the “infection” has been contained or it has been pervasive. Bootstrap percolation was first introduced in the late 1970s as a simple model to study the properties of some magnetic materials (Chalupa et al. 1979; Kogut and Leath 1981; Pollak and Riess 1975). One application that it was proposed to model was crystal field interactions, which tend to suppress

magnetic moments by forcing the atoms into their singlet state; they are then in competition with exchange interactions that favor the alignment of the magnetic moments of neighboring atoms. For the material to display macroscopic magnetic properties, exchange interactions must be everywhere locally dominant. Later it became apparent that the bootstrap percolation model is quite accurate in describing certain (low temperature) properties related to quadrupolar orientational ordering of molecular solids (Adler et al. 1987), for example, when both quadrupolar and isotropic molecules are present. A paradigmatic example is solid molecular (ortho-H₂)_x(para-H₂)_{1-x} or (para-D₂)_x(ortho-D₂)_{1-x} (Adler 1991; Adler et al. 1987). More recently bootstrap percolation, also called k -core percolation, has seen a resurgence of interest in connection to simple kinetic models for the glass transition (Fredrickson and Andersen 1984; Jäckle and Krönig 1994; Kob and Andersen 1993) and as a model system for jamming of both hard-sphere and soft-sphere molecules at high packing densities (Schwarz et al. 2006). Other applications have been suggested in the study of porous fluid flow through cracked rocks (Adler and Aharony 1988), disease spreading (Balogh and Pete 1998), hysteresis (Sabhapandit et al. 2002), computer storage arrays resilience to failure (Kirkpatrick et al. 2002), sand-pile formation (Manna 1998), spreading of alerts on distributed networks (Treaster et al. 2006), and many other problems for which standard nearest-neighbor percolation has already been proposed as a model system (Stauffer and Aharony 1992). More generally, bootstrap percolation is a useful model to address certain physical properties of a system whose local interactions are strongly contingent on the relative states of neighboring units, whereby a prevailing driving “force” only arises when many units act cooperatively “in phase.”

Introduction

In the decades that preceded the introduction of bootstrap (or k -core) percolation models, a new paradigm in statistical physics had revolutionized

our understanding of complex physical systems, especially in the presence of critical behavior and in its vicinity. From Ising onward (Ising 1925), simple (often lattice) models became an increasingly popular way to treat highly complex problems, analytically and later by means of computer simulations. In some rare cases highly nontrivial exact solutions (Onsager 1944) provided the first hint that (already in two dimensions) one would discover important connections with real critical behavior of continuous systems. Quite unexpectedly, given the simplicity of lattice models, it was later demonstrated that in the proximity of critical points a surprising variety of important and correct general results can be derived all within the framework of renormalization group calculations for lattice models (Wilson 1983). It emerged that in most cases dimensionality is the only relevant variable in play for systems belonging to the same universality classes. Thus, to rely on the use of lattice models was found to be much less problematic than one would have anticipated. The universality of behavior emerging from the study of criticality for simple lattice models was understood to apply under some very general conditions about the microscopic forces, as with short ranged interactions and if contributions from multi-body interactions were unimportant. Conventional (site or bond) percolation fits perfectly in this picture (Smirnov and Werner 2001; Stauffer and Aharony 1992), providing a way to investigate further the geometrical properties of systems with critical behavior that are characterized by the same universal exponents as those of critical phenomena. On the other hand, it represented a confirmation of the rather surprising ubiquitousness of scaling (Widom 1974) universality classes.

Bootstrap percolation provides an extremely useful platform to investigate other classes of phenomena. Can we construct a simple percolation model that produces other types of universality classes? In percolation theory, models that deal with exceptions to equilibrium continuous phase transition critical behavior are known to exist. Oriented and rigidity percolation are just some examples (Sahimi 1994). Bootstrap percolation is a model which has the flexibility to explore an ample spectrum of conditions over the local

“interactions” while still facilitating in many cases, through its simplicity, the development of rigorous mathematical results (Aizenman and Lebowitz 1988; Cerf and Cirillo 1999; Cerf and Manzo 2002; Holroyd 2003, 2006; Schonmann 1992; van Enter 1987; van Enter et al. 1990, 1991). The underlying “interactions” can be thought of as strictly local. However, over larger scales and unlike with critical phenomena, the results are strongly dependent on the specifics of the interactions, scaling can be sometimes problematic, and the outcomes can be quite diverse. Concurrently, bootstrap percolation can be viewed as a cellular automaton where basic dynamical properties of out-of-equilibrium or slowly evolving systems can be studied (Adler and Aharony 1988; Ertel et al. 1988; Jäckle and Krönig 1994).

Let us make one concrete example. To set the discussion into context, we can think of some of the several lattice models that have recently been proposed to describe some dynamical properties of glass-forming systems (Fredrickson and Andersen 1984; Jäckle and Krönig 1994; Kob and Andersen 1993) or jamming scenarios (Schwarz et al. 2006). These models can be of two kinds (Ritort and Sollich 2003): either lattice gas models in which the particle number is conserved (Ertel et al. 1988; Jäckle and Krönig 1994; Kob and Andersen 1993) or spin models of the Ising type (Fredrickson and Andersen 1984) in which some simple external field drives the equilibrium configurations to have low mobility at low temperatures. The distinction is not extremely important, similarly to the situation of Ising-like models for ferromagnetic transitions versus lattice models for liquid–vapor transitions. In any case, it is postulated that some particles can only move (or spins can flip) if the number of occupied neighbors (or of up-spins) does not exceed a given threshold number. Conversely, one may say that the dynamics is facilitated if a sufficient number of vacant sites (down-spins) exist in the neighborhood of a given particle to support the required density transformation. The outcome is clear. The dynamics are constrained locally in all-or-nothing possibilities, which depend on concentration of vacant (or mobile) space around. If

this vacant space is not sufficient, the dynamics does simply not progress. As a consequence collective motion can become heterogeneous and dramatically slowed (Fredrickson and Andersen 1984; Jäckle and Krönig 1994; Lawlor et al. 2005; Ritort and Sollich 2003).

Having such a picture in mind, we can immediately recognize the connections with bootstrap percolation (BP). In BP, the sites of the lattice can be either occupied with probability p or vacant with probability $q = 1 - p$. Usually, multiple occupancies are not admitted in such models, and the initial probability for occupied sites is entirely random, but such conditions are of a practical nature, and variants are admitted (Manna 1998). We can refer to p as either the concentration or particle density. The linear system size of the lattice is taken to be L . We then define a number $1 \leq k \leq z$, z being the coordination number. For convenience, let us also define $m = k - 1$ to make contact with several alternative definitions of the same parameter that are present in the literature. Then a culling process is carried out. All vacant sites as well as all sites that have k or more occupied sites among the nearest neighbors (the “constrained” sites) are left unaltered, while all sites that have m or less occupied neighbors among their nearest neighbors are removed. Step by step, many particles are removed and the concentration of particles gradually decreases. As new space is emptied, other particles previously stable can be removed. We eventually reach a stationary situation.

There can be different scenarios for the stationary state at the end of the culling process. There can be either no particles at all or there can be clusters of particles, one of which will eventually span the entire system (we shall see that in some cases there can be no finite-sized clusters, and the only two possibilities are that there be either no particles at all or a giant spanning cluster). The outcome depends on p , k , the lattice geometry, and on the system size L . For example, for not too small L , $k > 2$ and for small values of p we can expect that all particles will be eventually removed. A systematic study can be carried out using a similar procedure to that of conventional percolation. Given the system size L , the culling

process is carried out at some low value of p . It is expected that there will not be spanning clusters in the final configurations. p is gradually incremented, until at a certain value $p_c(L)$ that depends on L , 50 % of the final configurations will have a spanning cluster of irremovable particles. By changing the system size L we can construct the relation $p_c(L)$ between the bootstrap percolation finite-size critical concentration and the system size. For an infinitely extended system, we define $p_c = p_c(\infty)$ as the (“thermodynamic”) critical fraction. Alternatively, one can fix p and let the system size vary from small to large L and identify the critical size L_c , known as the bootstrap percolation length – this is the size of system for a given p for which 50 % of the configurations lead to a large spanning cluster in the final state. Then p is varied so that we can construct the relation $L_c(p)$ between p and the corresponding bootstrap percolation critical size L_c , which is of course just the inverse of $p_c(L)$. Other quantities of interest are the same of conventional percolation, such as the concentration of occupied sites in the clusters surviving the culling process, or the mass factor associated to the spanning cluster.

$p_c(L)$ and $L_c(p)$ can be clearly evaluated in a systematic fashion from computer simulations. Analytically there are radically different techniques that can be used to find them, depending on the value of k and the lattice geometry. For low k the bootstrap percolation problem is essentially equivalent to conventional percolation (Stauffer and Aharony 1992), and therefore real-space renormalization group calculations are the obvious choice. As we will see, there typically is some value of k , call it k_{uv} , at which “unstable voids” (Adler 1991; Adler and Aharony 1988; Adler and Lev 2003; Aizenman and Lebowitz 1988; De Gregorio et al. 2005; Kogut and Leath 1981; van Enter 1987; van Enter et al. 1990, 1991) emerge for any choice of $k \geq k_{uv}$. More precisely, while for $k \geq k_{uv}$ clusters of either finite size or spanning the system can survive the culling procedure, for any $k \geq k_{uv}$ self-sustaining (finite) clusters cannot survive the decimation process. This is typically due to the presence of voids that can become unstable when $k \geq k_{uv}$, i.e., are cores of empty sites of certain critical sizes that with high

probability can nucleate and lead to a complete decimation of the particles in the system. For such models, sophisticated analytical techniques have been devised and developed (Aizenman and Lebowitz 1988; Balogh and Bollobás 2003; Cerf and Cirillo 1999; Cerf and Manzo 2002; Schonmann 1990a, 1992), in some cases leading to explicit rigorous mathematical results (Holroyd 2003, 2006) or exact interpolations and predictions (De Gregorio et al. 2005). A third route is that of “mean-field” calculations for Cayley trees (Bethe lattices) (Chalupa et al. 1979; Harris and Schwarz 2005; Moukarzel et al. 1997; Schwarz et al. 2006; Sellitto et al. 2005). These have been investigated thoroughly in recent years especially because there can be values of the parameter k in the window between those values of k that can be treated with usual renormalization group techniques as in conventional percolation, and the value k_{uv} at which unstable voids are expected to arise. Some very interesting results have emerged already, in combination with simulations (Schwarz et al. 2006) and some generalizations of bootstrap percolation models (Jeng and Schwarz 2007; Toninelli et al. 2006, 2007). However, there still are some controversies that will have to be clarified (Parisi and Rizzo 2006). We expect that many of these issues will become clearer in the near future, possibly with new approaches (Harris and Schwarz 2005) that will not rely entirely on mean-field calculations (Chalupa et al. 1979). Finally, one obvious extension of bootstrap percolation is to random networks (Dorogovtsev et al. 2006; Goltsev et al. 2006), which we discuss in section “*k*-core Percolation on Random Networks” – this approach is already attracting considerable interest.

Bootstrap Percolation with $m \leq 2$

The case $k = 1$ ($m = 0$) is trivially the same problem as conventional percolation (Stauffer and Aharony 1992), in any dimension and for any lattice geometry. In fact, only isolated occupied sites are removed, which in any case do not participate to the construction of percolation clusters

in conventional nearest-neighbor percolation. It is then straightforward to recognize that, on approach to criticality, the critical fraction $p_c(L)$ is related to the system size and $p_c = p_c(\infty)$ via the relation,

$$|p_c(L) - p_c| = AL^{-1/\nu}[1 + \epsilon(L)] \lim_{L \rightarrow \infty} \epsilon(L) = 0 \quad (1)$$

while the total fraction of sites belonging to the infinite cluster vanishes with p approaching p_c from above as,

$$P_\infty \propto (p - p_c)^\beta \quad (2)$$

The exponents ν and β can be derived within real-space renormalization group calculations, or their relations derived from scaling theory, and estimated from computer simulations. They are therefore only dependent on the dimensionality d and not on the geometry of the lattice. All other exponents that are related to the mass fraction or to the percolation correlation length are dependent on the previous exponents and can be derived from those. Their values are given in this volume in the sections devoted to standard percolation.

In the case $k = 2$ ($m = 1$), only dangling ends are removed from the clusters of any size. It follows that this has no effect on the relation given in Eq. 1, representing correctly the relation between the concentration of particles and the size of the spanning cluster near the percolation transition. In regard to the other exponents relating the system size to the mass fraction or the probability that a site belongs to the spanning cluster, although not apparent from usual system sizes (Branco et al. 1984), it is found that the exponent β is also universal (Branco 1993; Chaves and Koiller 1995; Medeiros and Chaves 1997). That is, β coincides with β from standard percolation. This becomes only evident if the system sizes are very large (Chaves and Koiller 1995; Medeiros and Chaves 1997), and it is supported by general arguments (Branco 1993). It is noticeable that scaling arguments apply appropriately to both $k = 1$ and $k = 2$, and one has the usual picture of continuous phase transitions.

Sharp Thresholds: $m \geq d$ on Regular Lattices

The case that perhaps historically has attracted most interest in bootstrap percolation is when we pass from a picture of the type well described by the theory of critical points to one where “first-order” type transitions emerge. Typically, the precursor of such transitions is a very sharp threshold in the concentration-dependent probability to percolate, which is driven by the indirect effects of the so-called unstable voids (Adler 1991; Adler and Lev 2003; Aizenman and Lebowitz 1988; De Gregorio et al. 2004, 2005; Ertel et al. 1988; Jäckle and Krönig 1994; Kob and Andersen 1993; van Enter 1987; van Enter et al. 1990, 1991). These are special objects whose interior is void of particles. They have the potential capacity to eat away all the particles in the system, provided that they manage to grow beyond a certain threshold size. We can say that if their spreading is not contained at an early time, they will almost certainly end up “invading” or “infecting” the entire system. Whether there is any such object in the system depends of course on the initial concentration of occupied and vacant sites and on the system size (if the system is finite in size). Their properties will be discussed extensively in this section. One interesting aspect of these models is that their studies have been characterized by an intriguing series of twists and turns, before a clearer and more thorough picture would finally emerge.

The simplest case in which dominance of unstable voids can emerge is when $m \geq d$ ($k \geq d + 1$) on regular lattices. Therefore, $m \geq 2$ for the square lattice, $m \geq 3$ for the simple cubic. However, other geometries can also lead to the same situation, and d might not always be the relevant threshold value for separating the different classes. For example, the same picture holds for the triangular lattice (the two-dimensional lattice with coordination number $z = 6$), whereby unstable voids will emerge if $m \geq 3$. Notice that for the triangular lattice, the threshold number for this class is 3 and it also coincides with $z/2$, as it does for the square lattice, and in general for the hypercubic lattice.

First, we shall be discussing informally some general preliminary properties in the case $m = d$ for regular lattices. Next, some of the known results will be outlined. Finally, some of them will be discussed more extensively with some derivations.

Spanning Clusters: $m = d$

Let us take the case $m = 2$ on the square lattice (i.e., $k = m + 1 = 3$). This implies that only particles with less than three occupied neighbors can be removed. To start with, it is useful in general to know whether clusters of finite size (i.e., nonspanning) might survive the decimation process in the box of area L^2 . Let us suppose that one such cluster exists. By definition, if it is finite, the cluster must have a boundary. But if it has a boundary, this implies that there exists a nonempty set of particles in such cluster that have at least two vacant sites as their nearest neighbors. This set cannot be empty because any finite cluster is a compact object (you may think that it has at least four “corners,” or vertices). Particles in such set are therefore removed at the next iteration of the culling process. But now we have again a finite cluster with a nonempty set of “corners.” It follows that the removal procedure cannot be stopped and the cluster will eventually be washed away. We conclude that the only possibility for a cluster to survive the culling process is that it is not self-sustaining, i.e., only spanning clusters that are connected to themselves through the lattice boundary lines may exist at the end. Similar conclusions can be derived for any dimension for the simple cubic and hypercubic lattices.

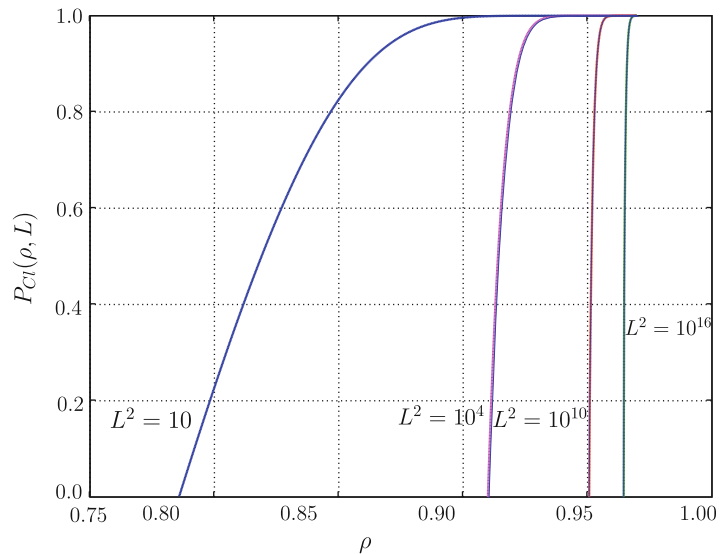
It should start to transpire already why these models are special. Given a certain system size L and some value of p , after culling terminates only two situations can happen. Either the lattice is empty or it contains one large (massive) spanning cluster, and we collect the statistics for many equivalent realizations at L and p . We cannot, as in the case of critical points in conventional percolation, identify a broad distribution of finite-sized clusters of all lengths, whereby each sampled configuration (whether percolating or not) would be similarly distributed in any element from the

wide samples. Furthermore, from the above argument it is also clear that all the “roughness” over the boundaries of any set of connected particles in the spanning cluster is washed away during the culling process. In other words, we should expect its fractal dimensionality to be the same as the volume it is embedded in. All these qualitative considerations suggest a scenario that is very typical of first-order phase transitions rather than that of continuous ones. More careful examinations are consistent with this picture. These models are without doubt a departure from standard percolation problems and also from bootstrap percolation models with small values of m .

In Fig. 1, we see an example of the probability of a spanning cluster in the final configuration, plotted as a function of particle concentration p and for different system sizes (from theory and for a modified model that is qualitatively equivalent to the two-dimensional $m = 2$ square lattice model). As we can see, the “transition” in the probability, from essentially zero to some finite value, occurs over a very narrow range, and it displays an important size dependence. At large system sizes the sharp change is “almost” discontinuous. Furthermore as said, whenever a spanning cluster survives the culling process, the fraction of occupied sites in

it is typically finite (i.e., nonfractal), leading to a similar sharpness in the probability that any given site anywhere in the lattice belongs to the spanning cluster. The analysis of similar results in two and three dimension from computer simulations (which are limited as to the maximum system size available) led initially to the conjecture of a power-law behavior (Kogut and Leath 1981) for $d = 3$, in the form of Eq. 1 but with a critical concentration lower than that of the discontinuous jump, and it was not excluded that the critical concentration for an infinitely extended system would have been $p_c < 1$. This premature conjecture was only partially and very qualitatively consistent with the mean-field Bethe lattice behavior (Chalupa et al. 1979) studied theoretically (this topic will be discussed in another section). However, it was later rigorously proven that $p_c = p_c(\infty) = 1$ (Aizenman and Lebowitz 1988; Schonmann 1992; van Enter et al. 1990, 1991). More precisely, as we will see, the probability that an unstable void develops is always small but strictly positive, for any initial value of $p < 1$ and in any dimension for regular lattices, whenever $m \geq d$. Therefore, if we suppose that the lattice is infinitely extended, we will encounter at least one unstable void with certainty.

Bootstrap Percolation,
Fig. 1 The typical probability P_{CI} that a spanning cluster survives the bootstrap process as a function of particle density and for different system sizes. Two-dimensional modified model in the example. From left to right, system sizes correspond to $L^2 = 10$, $L^2 = 10^4$, $L^2 = 10^{10}$, and $L^2 = 10^{16}$



Void Instability and Rigorous Results

In recent years more and more rigorous, theoretical and simulation results have led to an impressively detailed understanding of these models (Adler 1991; Adler and Lev 2003; Adler and Stauffer 1990; Adler et al. 1989; Aizenman and Lebowitz 1988; Balogh et al. 2012; Balogh and Bollobás 2003; Cerf and Cirillo 1999; Cerf and Manzo 2002; De Gregorio et al. 2004, 2005; Holroyd 2003, 2006; Holroyd et al. 2004; Kurtsiefer 2003; Schonmann 1992; van Enter et al. 1990). Before stating some of these results we first define, for convenience, a variant model that has been described in great detail. It is called the modified bootstrap percolation model (De Gregorio et al. 2004, 2005; Holroyd 2003, 2006; Schonmann 1992). For any regular lattice, any particle can be removed if and only if in any of the coordinate directions, it is neighbored by *at least* one vacant site. This condition is similar to the case.

We can now look into some of the known rigorous results. They are listed here as relations between the threshold concentrations for the first appearance of a spanning cluster, as functions of the system size L . This is the commonest way to visualize quickly the types of finite-size corrections. However, later we will discuss why for other purposes not necessarily this is the most convenient form. The inverted form of these relations will be discussed later. In all the following, $\epsilon(L)$ must be intended as an unspecified, *nonuniversal* (positive or negative) function that is vanishing in the limit $\lim_{L \rightarrow \infty} B(L)$ is some positive term which is certainly bounded by two constants for sufficiently large L . We have for all regular lattices from square to hypercube,

$$p_c(L) = 1 - \frac{\pi^2}{18 \ln L} [1 + \epsilon(L)]$$

$$d = 2, m = 2 \quad (\text{Holroyd 2006}) \quad (3)$$

$$= 1 - \frac{\pi^2}{6 \ln L} [1 + \epsilon(L)]$$

$$d = 2, \text{ modified (Holroyd 2006)} \quad (4)$$

$$= 1 - \frac{B(L)}{\ln \ln L} \quad d = 3, m = 3$$

$$(\text{Aizenman and Lebowitz 1988; Fernholz and Ramachandran 2003}) \quad (5)$$

$$= 1 - \frac{\pi^2}{6 \ln \ln L} [1 + \epsilon(L)]$$

$$d = 3 \text{ modified (Holroyd et al. 2004)} \quad (6)$$

$$= 1 - \frac{B(L)}{\ln^{o(d-1)} L} \quad \text{any } d \geq 2,$$

$$m = d \quad (\text{Bringmann and Mahlburg 2012}) \quad (7)$$

$$= 1 - \frac{\pi^2}{6 \ln^{o(d-1)} L} [1 + \epsilon(L)]$$

$$\text{any } d \geq 2, \text{ modified (Holroyd et al. 2004)} \quad (8)$$

$$= 1 - \frac{B(L)}{(\ln L)^{d-1}} \quad \text{any } d \geq 2,$$

$$m = z - 2 \quad (\text{Aizenman and Lebowitz 1988}) \quad (9)$$

$$= 1 - \frac{B(L)}{(\ln^{o(2d-m-1)} L)^{m-d+1}}$$

$$\text{any } d \geq 2, d \leq m \leq 2d - 2 \quad (10)$$

$$(\text{Bringmann and Mahlburg 2012; Ertel et al. 1988})$$

As usual, z is the coordination number, $z = 2d$ in this case. The expression $\ln^{o(n)}$ stands for the natural logarithm iterated n times. The explicit form of $\epsilon(L)$ is expected to vary considerably case by case, nevertheless it vanishes for large L , but it is unknown rigorously. From expressions from Eqs. 3, 4, 5, 6, 7, 8, 9, and 10 we readily recognize the importance of finite-size effects. To see this, take, for example, the general expression for $m = d$ outlined in Eq. 7, which is in fact the case of major interest. The leading term in the expression is the inverse of the logarithm iterated $d - 1$ times, which converges to zero extremely slowly, the higher the dimension the slower it converges. This is very different from standard power-law behavior and explains why it was not

immediately recognized that these systems have a critical concentration of 1. As it transpires, we have a whole new “universality class,” peculiar to bootstrap percolation. It is especially noticeable that in many cases, the asymptotic expressions are such that the multiplicative constant is known exactly. Another issue that may not appear so obvious at first is that the forms of $\epsilon(L)$ are not always rigorously known. Due to the slow convergence of the leading terms, $\epsilon(L)$ may add substantial finite-size corrections that are in addition to the iterated logarithmic part. In fact, in principle $\epsilon(L)$ in itself may converge to zero even slower than inverse logarithms, and it may be comparable to unity up until the largest sizes that are physically interesting. As we are going to see, already in two dimensions this effect is not at all negligible.

As we shall see, a more natural choice for these models is to express the critical bootstrap length in terms of the initial particle concentration or rather of the initial concentration of empty sites $q = 1 - p$. There is a unique transformation from $q = q(L)$ to the inverse relation $L = L(q)$ that relates critical concentrations to critical sizes and vice versa. For example, we can preliminarily rewrite Eq. 7 as expressing the asymptotic result $L_c(q) \sim \exp^{o(d-1)}(A/q)$, i.e., an iterated exponential whose argument is of order $O(1/q)$. Therefore in $d = 2$ we have

$$L_c(q) \sim \exp\left(\frac{A}{q}\right) \quad (11)$$

expressing the exact dramatic divergence of the critical size when the fully filled lattice limit is approached. It is useful, however, to formally invert Eqs. 3 and 4 by separating out the asymptotic contribution from the corrective term and by defining an unknown function $f(q)$ related to $\epsilon(L)$. We can do this by writing

$$\ln L = \frac{A}{q} + f(q)$$

and observing that

$$\epsilon(L) = \frac{qf(q)}{A} \quad (12)$$

must hold. Notice that $A > 0$ and therefore $f(q)$ and $\epsilon(L)$ are of equal sign. From Eqs. 3 and 4 and the properties of $\epsilon(L)$, in the limit $L \rightarrow \infty$ both $q \rightarrow 0$ and $\epsilon(L) \rightarrow 0$, and therefore,

$$L_c(q) = \exp\left[\frac{A}{q} + f(q)\right] \quad (13)$$

$$\lim_{q \rightarrow 0} q f(q) = 0 \quad (14)$$

As we can see, $f(q)$ may in principle be a divergent function with vanishing q , although it must always diverge slower than $1/q$. Indeed, the observed critical bootstrap percolation size is often orders of magnitude off from the expected leading asymptotic behavior (Adler 1991; Adler and Lev 2003; De Gregorio et al. 2004; Holroyd 2003). This subtlety will be briefly discussed later.

How can we derive Eq. 11 in $d = 2$ and the corresponding iterated exponentials for $d > 2$? First, we expand more explicitly on the concept of unstable voids (or critical droplets). To illustrate an elementary example of what an unstable void is, take the trivial case $m = z - 1$, i.e., all occupied sites with at least one vacant neighbor are removed. Take a large lattice with a certain distribution of particles $p = 1 - q < 1$, and p very close to 1 (i.e., q very close to zero). If $L^d \gg 1/q$, we can be certain that there would be some empty sites in the system (despite q being small). According to the rule assigned, such voids will gradually expand and eat away all the particles in the system, without any barrier that may stop them from growing. Isolated voids are therefore always “unstable” when $m = z - 1$, they start to grow immediately as soon as the culling process is started, and they cannot be stopped. Furthermore, if starting from the same initial configurations we subdivide the system into many subsystems of volume L' such that $L'^d \ll 1/q \ll L^d$, we end up with many separated subsystems entirely filled, and a very few containing one (or more) vacant sites. After the

culling process is implemented separately on each one of the subsystems, a tiny fraction of the total number of them (those with vacant sites, i.e., unstable voids) are completely empty. All the others are entirely filled by particles. We thus see how in the presence of unstable voids, for a given value of $p = 1 - q$ we can have different scenarios, depending on the system size, while at the same time for an ideal system that is infinitely large, any $p < 1$ leads to all space to be empty after bootstrap.

The situation is of course much more complex in the more interesting cases, but some basic principles are unaltered (in a crude sense). Let us consider the case of the square lattice when $m = 2$ or consider the modified model (they behave similarly). Imagine that we have created somewhere a rectangle whose inside is completely empty (note that it is often said that such rectangle is internally spanned, but we must not confuse this notion with that of a spanning cluster of percolating particles). In Fig. 2, we have a square as an example. On the boundary lines of its perimeter there can be any number of particles. But let us see what can happen if some sites on those lines are vacant. Due to the rules for the removal of particles, any vacant site on any one of those lines is a one-dimensional unstable void limited to that line, because each site on the line has already one vacant neighboring site which lies in the interior of the empty square. This means that if on any of the boundary segments there is one vacant site or there are more, that segment will be vacated. If the condition is satisfied in all four directions, the empty square can engulf its boundary and become two linear units larger per side. Again, let us consider $p < 1$ but very close to 1, i.e., q positive but very small. For small squares with side length much smaller than $1/q$, it is very unlikely that any such empty square will grow further. However, for side lengths much larger than $1/q$ the opposite is true, it is almost certain that the square will grow to the next step and to the steps after (as the side length becomes larger, it is increasingly likely that the boundary lines will be unstable with respect to the internal empty square). Voids of the first type are therefore stable, and voids of the second type are expected to be

unstable. Therefore, when we turn our attention back to the entire lattice of size L , we can be certain that all particles will be removed provided that L is large enough so that the lattice contains one or more unstable voids (and so the lattice is sometimes said to be internally spanned by the voids. Again such terminology must not be confused here with spanning clusters of particles). In order to determine whether voids can ever become unstable even for very small q , we must determine rigorously some bounds for their probability to arise.

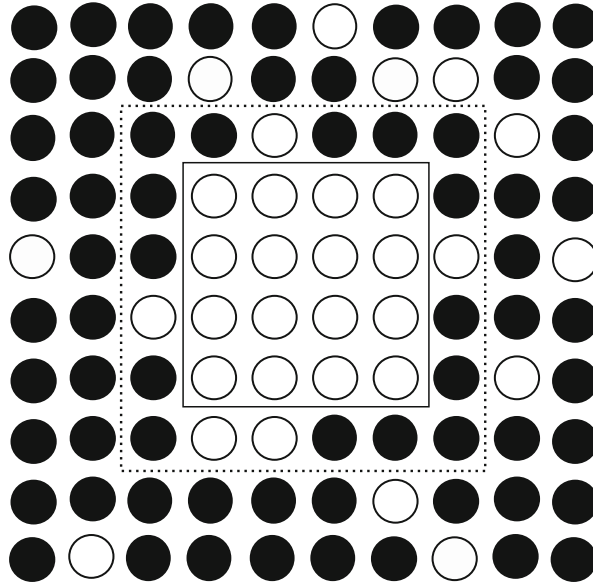
To quantify this argument, we ask what is the probability that a vacant site can nucleate and grow indefinitely? By letting this process proceed via the formation of larger and larger squares we certainly obtain a lower bound to the nucleation probability (it is a lower bound because, more generally, nucleation can also proceed via rectangular voids of various elongations (De Gregorio et al. 2005)). Given an empty square of side length l , the probability that any of the four external boundary lines can be vacated coincides the probability of there being at least one vacant site, which is formally given by $1 - p^l$. (it is the complement of there being l particles, which is p^l from the random measure distribution on p). The joint probability for all four sides *at the same time* is $(1 - p^l)^4$. Let us call the probability of indefinite nucleation v , and $v_b < v$ is some lower bound. To evaluate this bound, we may start with a square of size 2×2 as the nucleus. We may write,

$$v_b = q^4 \prod_{k=1}^{\infty} (1 - p^{2k})^4 \quad (15)$$

Here, k is the side length of the growing square (which is an even number at each step). Therefore,

$$\ln v_b = 4 \ln q + 4 \sum_{k=1}^{\infty} \ln(1 - p^{2k}) \quad (16)$$

To bound the sum we first expand the logarithm in infinite series and we exchange the order of summation. We then use the inequality $(1 - p^{2k})/p^{2k} > 2k(1 - p) = 2kq$.



Bootstrap Percolation, Fig. 2 Unstable voids in the square lattice. The internal 4×4 square delimited by the solid line has been vacated previously. Both in the modified and in the conventional $m = 2$ model, the square can engulf its four next sides leading to the vacation of the 6×6 square delimited by the dotted line. From there, the growth by squares in the modified model would be stopped because of the impossibility to proceed in the west direction, while the growth by squares is still allowed in the

conventional model up to the vacation of the largest 10×10 square in the figure. Finally, allowing for the growth by elongated rectangles in the modified model, the void can momentarily expand in the north, east, and south direction before all particles in the east direction can be vacated too. Differently from the squares-only process, this time the largest 10×10 square in the figure will be vacant at the end, also in the modified model

$$\begin{aligned} \sum_{k=1}^{\infty} \ln(1 - p^{2k}) &= - \sum_{k=1}^{\infty} \frac{1}{k} \frac{p^{2k}}{1 - p^{2k}} > - \frac{1}{2q} \sum_{k=1}^{\infty} \frac{1}{k^2} \\ &= - \frac{\pi^2}{12q} \end{aligned} \quad (17)$$

The last equality comes from Euler's sum which equals $\pi^2/6$ (one can also show that when $q \ll 1$ the inequality above is essentially an equality but for unimportant corrective terms). From Eqs. 16 and 17, we therefore have a new bound for the overall nucleation probability, meaning,

$$v > q^4 \exp\left(-\frac{\pi^2}{3q}\right) \quad (18)$$

Equation 18 shows that the nucleation probability, i.e., the probability that unstable voids exist, is a strictly positive quantity for any $q > 0$. This implies that for any system of size $L^2 v_b \gg 1$,

i.e., $L \gg q^{-2} \exp(\pi^2/6q)$, we can be almost certain that no particle can survive decimation. As $q \rightarrow 0$ ($p \rightarrow 1$), the required L increases dramatically. Perhaps even more surprising is if we look at the latter expression, and compare it with Eq. 4, valid for the modified model. The two are fully consistent, with the correct constant. This is surprising because we started with a bounding argument and, apparently, we have ended up with the correct estimation of the asymptotic expression (at vanishing q) for v and L_c . The proof that in fact the bound described above does furnish the correct asymptotics for both v and L_c is highly nontrivial (Holroyd 2003), and despite it being a relatively recent result, it is already a cornerstone of bootstrap percolation. One needs to calculate an upper bound which is, to the leading asymptotic order, coincident with the lower bound. In regard to the conventional (non modified) $m = 2$ case, the argument employed for bounding v starting from the probability of growing square-like

unstable voids can be refined. In that case, even if one boundary line is entirely filled with particles, one or more vacancies present in the adjacent line can also lead to all particles in both lines to be vacated (this is seen with the help of Fig. 2). This necessitates some technical adjustments in the calculation above in Eq. 15, but the rest of the argument remains unchanged (Holroyd 2003). One gets a new bound for the square-like process that is precisely in the form (Eq. 18) but with a new constant given by $\pi^2/9$. Again, by means of the identification $L_c^2 \sim v^{-1}$ for the critical size (part of the demonstration (Holroyd 2003) shows that to be not forbidden at $q \ll 1$, and simulations are consistent already at not too low q (De Gregorio et al. 2004)), we have an expression consistent with Eq. 3. The complete proof for the upper bound is essentially equivalent to that for the modified model. In general, the modified model renders some of the calculations more straightforward, but the two models are in essence very similar.

We thus learn that Eq. 11 (or more appropriately (Eqs. 13 and 14)) is a rigorous result, with the calculated constants A equal to $\pi^2/6$ and $\pi^2/18$ for the modified and conventional $m = 2$ case on the square lattice, respectively. It would appear that we have at last gained a correct and complete picture, with exact rigorous mathematical results (Holroyd 2003) that we can finally compare with computer simulations (KurtSiefer 2003) with a sufficient degree of confidence. However, this is not quite as true yet (Adler and Lev 2003; De Gregorio et al. 2004). In reality, fits that use Eq. 11 are typically consistent with estimated constants that are sensibly different (Adler and Lev 2003; Adler et al. 1989) from the ones calculated within the theory (by factors as large as 2 or 3). This puzzle will be discussed in the next section. It has to do, as earlier pointed out briefly, with the more general expression in Eqs. 13 and 14 and its subtle implications.

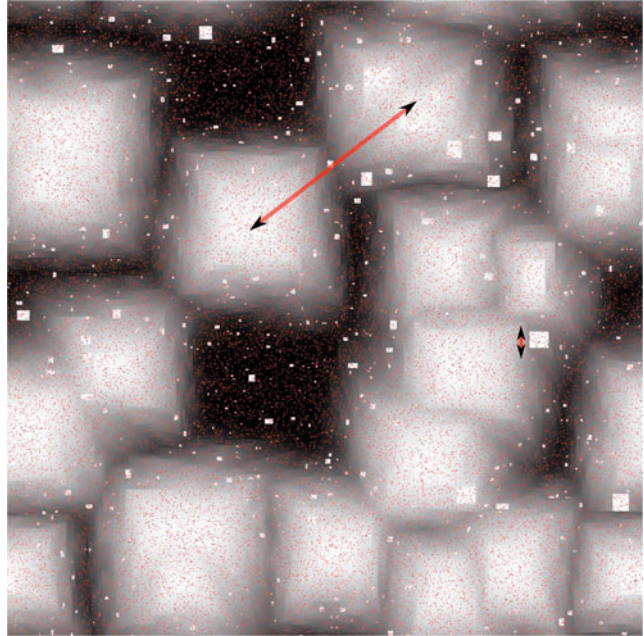
As we have seen, there is a nonzero probability to encounter unstable voids at any $q > 0$ ($p < 1$). When $q \ll 1$, voids can become unstable once they reach a side length much larger than of order $\bar{k} \sim O(1/q)$ (a more rigorous estimate lends $\bar{k} \sim O(\ln q / \ln p)$). To appreciate this statement qualitatively, we observe that the probability

$1 - p^k$ that a boundary line can be wiped out by the growing void is of order $1 - \exp(-b) \sim 1$ if $k = b/q$, $b \gg 1$, and $q \ll 1$ (notice that the latter also implies $q \approx -\ln p$). Consequently, if on the one hand for $k \ll O(1/q)$ the voids are stable with high probability, on the other hand for $k \gg O(1/q)$ they are unstable with high probability. The length $\bar{k} = 1/q$ is a novel length not present in standard percolation models with critical points (see Fig. 3). We see that contrary to those models, we might be in serious trouble if we were to assume that we can freely rescale the lattice spacing by any finite factor (like in a self-similar spin-block picture of the type of Kadanoff), just as long as the scaling length is much smaller than the longest length. Here instead we have the larger length-scale $L_c(q)$ which is always sensibly much greater than the length-scale $\bar{k}(q)$, for small q . On the other hand, on a practical scale, this feature can be of tremendous advantage. Indeed, it is sometimes sufficient to determine the properties of some physical quantities (e. g., correlations) up to within the distance $\bar{k}$ and no further, when $L_c \gg \bar{k}$. A good example is when we want to evaluate the nucleation probability v . Rather than sample systematically systems of very large sizes, it is sufficient to determine whether some nuclei can grow further than $\bar{k}$ (De Gregorio et al. 2004), and what the associated probability is for a given concentration p . This saves an enormous amount of computer running time for values of p that correspond to very large critical bootstrap lengths.

More articulated mathematical analysis lead to bounds and exact results in higher dimensions (Cerf and Cirillo 1999; Cerf and Manzo 2002; Holroyd 2006). We can consider a qualitative argument to determine the bootstrap critical system size in more than two dimensions. As an example, let us consider $d = 3 = m$ (also modified model). We need to establish whether voids can be unstable in this case, and this is indeed the case. Take, for instance (van Enter et al. 1990, 1991), some large cube all empty in the inside and whose side length is of some value k . We look for a condition such that the empty cube can grow in a given direction by one step, thus absorbing any particle that might eventually lie within the boundary surfaces. In the simple case,

Bootstrap Percolation,

Fig. 3 Evolution of the bootstrap process for $k = 3$ in $2D$ ($p = 0.952, L = 900$). The time at which particles are removed is depicted by the color – the first ones removed are *white* and the last ones removed are *black* (initial vacancies are *red*). It is seen that the bootstrap removal process starts at nucleation centers, also called connected holes. The *larger scale* indicated in the figure is the bootstrap length $L = 1/\sqrt{v}$ or the typical distance between connected holes. The *shorter scale*, $\bar{k} \sim 1/(1-p)$, is the critical length above which voids will become unstable



we consider one square-like boundary surface per side at a time. The sites on one single surface form a $k \times k$ square lattice, but additionally each site is also connected to one site that lies on the interior of the cube (which is certainly empty), and one on its exterior. Thus any site within such $k \times k$ square lattice that forms the boundary surface of the cube has at least one neighboring vacant site (because the cube is empty) and only needs two more vacant neighbors to be removed. A sufficient condition is that the two required vacant sites are among the four neighbors that lie on the $k \times k$ square lattice itself, irrespective of the occupation state of any site from the exterior. We thus realize that if locally the boundary $k \times k$ square lattice has at least one unstable void in the $m = 2$ sense, then the entire square can be vacated. This can be repeated for any of the six sides that form the entire boundary of the cube. It follows that we have reduced the treatment of the one-step growth for the empty cube for $m = 3$ to six equivalent $m = 2$ subproblems on its surface. A problem that we already know how to solve nevertheless. For example, at $q \ll 1$, we know that if the side length k is of order $\exp[O(1/q)]$, then with high probability all particles within the square-shaped surfaces are likely to be removed.

But this means that the empty cube will almost certainly grow by one step, and the same will happen at the next step. We have therefore established that, very approximately, we must expect the new $\bar{k}$ to equal $\exp[O(1/q)]$ in the present case (much larger than $O(1/q)$ as for the square lattice).

All that is left is to evaluate the probability that such unstable void of the required length arises somewhere. In principle, we would need an iterative formula of the type of Eq. 15, but it will suffice to determine a qualitative bound for that probability. A minimal condition for a cubical region at $q \ll 1$ to be unstable is that it must contain $\exp[O(1/q)]$ empty sites at least, in some appropriate positions. For example, if the six faces that constitute the frame of a cube are all empty, one can prove that the interior of the cube will be eaten away gradually, leading necessarily to an entirely empty cube of side length $\exp[O(1/q)]$, which is unstable for the argument above. This can happen with probability

$$q^{\exp[O(1/q)]} = \exp\{-\exp[O(1/q)]\ln(1/q)\}.$$

We then apply the usual condition that L_c^d multiplied by such probability be $O(1)$, and we get

$$L_c \sim \exp\{\exp[O(1/q)]\ln(1/q)\}.$$

By taking twice the logarithm, we first neglect $\ln \ln(1/q)$ compared to $O(1/q)$, and we then obtain

$$q \sim \frac{1}{\ln \ln L_c}$$

which is the desired result as in Eqs. 5 and 6. Rigorous results for upper bounds require other elaborate treatments, not to be mentioned here. However, as above, in most cases a convenient scheme for the proofs requires one to employ some dimensional induction from $d-1$ (supposedly known) to d (Cerf and Manzo 2002). It is worth noticing that an (elaborate) induction argument on dimensionality also allows one to derive Eq. 6 from Eq. 4 (Holroyd 2006). Similar arguments (alongside with their sophisticated rigorous counterparts) apply to dimensions higher than 3, giving rise to the iterated exponential (for $L_c(q)$) and iterated logarithmic forms (for $q_c(L)$) present in Eq. 7.

A word of caution, however, is in order here. The results so far have been illustrated assuming that d is kept fixed. From Eq. 7, which is valid for $m = d$ on the hypercubic lattice, we see that every time we raise d , the required L for attaining an arbitrarily small $q_c = 1 - p_c$ must increase, because each time we must add another iteration of the logarithmic function in the denominator. What happens then if we let d vary at the same time as varying L ? One notices that in reality Eq. 7 holds not only when d is fixed but also when it is some extremely slowly growing function of L (Balogh et al. 2007; Cerf and Manzo 2002). And so we ask if it is always guaranteed that q_c becomes arbitrarily small when d grows too (provided that L is large enough)? This must be answered in the negative (Balogh et al. 2007). In fact, there exists some monotonic $d = d(L)$ such that in the limit of $L \rightarrow \infty$ we have $q_c = 1/2 = p_c$. It is important to notice that $d(L)$ is still a very slowly growing function of L , more precisely $d(L) = (\ln \ln L)^2 \ln \ln \ln L$, but nevertheless it is sufficient for the result. In other words, there certainly exists a severe bound on how fast L must grow when d is

systematically raised, in order that we still have $p_c = 1$ for the system of infinite size. If the condition is not met, then $p_c < 1$ ($q_c > 0$) for a diverging L .

To complete this survey, we mention briefly the case $m = z - 2$ (Aizenman and Lebowitz 1988) where we have relations that are described in Eq. 9. The simplest case is when $m = 4$ for the simple cubic lattice. One can derive a bound by a recursion formula similar to Eq. 15, with partial probabilities of the type p^k in Eq. 15 now substituted by p^{k^2} (or more generally $p^{k^{d-1}}$ in d dimensions). To see this, consider the simple cubic model with $m = 4$ and the instability condition for cubic voids. We can reiterate an argument similar to (and yet simpler of) the argument above. If in any of the six boundary surfaces there lies at least one vacant site, then the empty cube can grow in that direction. If all six surfaces satisfy the condition, the whole cube will grow in all six directions concurrently. If the side length is given by k , the probability that one boundary surface is entirely filled with particles is given by p^{k^2} , and the complement is therefore $1 - p^{k^2}$, i.e., the probability that there lies one vacant site at least, or more. Rather than employing a full calculation (lengthy but trivial) for the bound such as the one in Eq. 15, we recognize that this situation is similar to the case $m = 2$ on the square lattice. There the critical size for the instability of the voids had to satisfy the condition $kq \gg 1$, i.e., with high probability there are vacant sites on the line. Here we have that a similar condition must hold, more precisely that $k^2 q \gg 1$ must hold. We therefore have, roughly, that $\bar{k} \sim 1/\sqrt{q}$ is the threshold size for voids' instability. By analogy with that case, we conclude that $L_c \simeq O(\exp(1/\sqrt{q}))$, in accordance with Eq. 9.

Additionally, some authors (Balogh and Bollobás 2006) have studied the behavior of isolated hypercubes for $m = d - 2$, for large values of d , showing that the critical concentration of empty sites sharply decays to 0 as $q_c \sim 2^{-2\sqrt{d}}/d^2$.

We conclude this survey on models with sharp thresholds by noticing that variants of bootstrap percolation may entail lengths that are diverging comparatively more severely than

those outlined in this section, on approach to the critical point $q = 0$. One example is the square lattice with the asymmetric rule introduced by Gravner and Griffeath (1996). The neighborhood is extended to two additional sites, the second neighbors that lie, for example, on the horizontal directions. The total number of relevant neighbors is therefore $4 + 2 = 6$, the four nearest and two second-nearest neighbors. The value of m is taken to be $m = 3$. One finds (van Enter and Hulshof 2007) that at $q \ll 1$, $L_c \sim \exp[O(1/q) \ln^2(1/q)]$. This is the same asymptotic behavior (Mountford 1995; van Enter et al. 1990, 1991) as in another asymmetric bootstrap percolation model on the square lattice introduced by Duarte (1989). Only three out of four nearest neighbors are considered each time, and particles are removed if at least two of those neighbors are empty. An even sharper transition was found earlier for a special variant of the bootstrap model on the square lattice (Schonmann 1990b). In this model, occupied sites can be removed as usual, but at the same time empty sites can also become occupied. The rule is therefore not strictly irreversible. At each iteration, any given site adjusts its state so that it conforms to the occupancy state of the majority of its neighbors. The key ingredient for the model is the assignment of a bias in all cases in which there is a parity situation, i.e., two neighbors are occupied and two are vacant. There is no majority, and to determine which state a site has to take, a bias is introduced towards one of the two possibilities. For example, we can codify the rule so that, for all parity situations, the site is removed with probability $y > 1/2$, and it becomes occupied with probability $1 - y < 1/2$. Therefore, when two neighboring sites are empty and two are occupied, at the next step the site will become empty with a higher probability than to become occupied. In this case, for every choice of $y > 1/2$, $p < 1$, and for large enough system sizes, there is a high probability that the final state will be an empty lattice. The critical system size scales (Schonmann 1990b) as $c_1(y)/q^2 < \ln L_c(q; y) < c_2(y)/q^2$, where c_1 and c_2 are two unknown constants that depend only on y . In other words, in this case $L_c \sim \exp[O(1/q^2)]$.

Corrections to the Asymptotic Behavior in the Presence of Unstable Voids

Typically, for the models that have a critical bootstrap length that grows exponentially or super-exponentially in $1/q$, a detailed comparison of computer simulations inferences with rigorous mathematical results is unsuccessful (Adler and Lev 2003; Kurtsiefer 2003). For the two-dimensional models, conventional $m = 2$ or modified, the constant A of best fit from the expression in Eq. 11 differs sensibly from the expected values derived from Eqs. 3 and 4, which are mathematically rigorous (Holroyd 2003). As an even more concerning issue, it has been suggested that the best fits can sometimes be obtained from different functional expressions altogether. For example, in three dimensions, on the one hand, we have the relation (Eq. 5) that implies that we should expect the best fits to L_c to be in the form $L_c \sim \exp \exp A/q$, the closer we approach $q = 0^+$ the better the fit. Contrarily to common intuition, however, it was proven from computer simulations (Kurtsiefer 2003) that for the largest sizes and the smallest q available a fit in the form $L_c \sim \exp \exp A/q^2$ is far more reliable, the closer we are to $q = 0^+$ the better the fit is compared to the expected $L_c \sim \exp \exp A/q$. At first sight this could erroneously be interpreted as a mere failure of either mathematicians or simulators. However, this does not need be the case. Take for example the two-dimensional case. If we look carefully at what the asymptotic results really mean, we have two equivalent ways of expressing them in general terms. One is as in Eqs. 3 and 4, and the other one is the equivalent form Eq. 13, provided that Eq. 12 holds. From the rigorous analytical arguments usually employed we have no way (as yet) to infer the exact form of either $\epsilon(L)$ or $f(q)$. We know, however, that $\lim_{L \rightarrow \infty} \epsilon(L) = 0$ and $\lim_{q \rightarrow 0} f(q) = 0$. However, $f(q)$ might still be a diverging function of q in the limit $q \rightarrow 0^+$, albeit not as fast as $1/q$. Plus, $f(q)$ enters Eq. 13 exponentially. This is worrying because it implies that the resulting discrepancy between Eqs. 13 and 11 may be in the region of orders of magnitude, and indeed it is (De Gregorio et al. 2004).

A natural question arises. Where did we lose track of all such nonasymptotic corrections? We may start looking backward at all the derivations and see where we might have made too gross assumptions. One of the main suspects is a relation that we have used all throughout in the discussion, although without rigorous proofs of its legitimacy but rather tacitly assuming its general validity. Given the probability v (also called the “connected hole density” (De Gregorio et al. 2004, 2005; Lawlor et al. 2005)) that a vacant site can nucleate indefinitely (i.e., that it becomes an unstable void), we have repeatedly inferred that the relation $L_c^d v \simeq 1$ holds reliably. Indeed, this is not strictly true in general. It tacitly assumes that the successful nuclei are not correlated spatially in any important way. On the other hand, at high concentrations of particles such nuclei become very rare and therefore highly contingent on the specific distribution of particles and vacancies in their surrounding, meaning that the probability to find one nucleating center just a few lattice spacings away from another one is extremely low. Even if we were to assume that there is a typical average number n of nucleating centers that occasionally tend to stick together, the consequent correction to the usual assumption $L_c^d v \simeq 1$ would be just a number, a factor of order n (eventually depending slowly on p). Hardly something that would account for order of magnitudes anyway. The good news is that v is a quantity that is directly accessible from simulations, more efficiently than L_c indeed (De Gregorio et al. 2004; Lawlor et al. 2005). It is therefore possible to compare v to direct estimates (Adler and Lev 2003; KurtSiefer 2003) of $1/L_c^d$ and operatively test the relation $L_c^d v \simeq 1$. Wherever comparisons have been made the two are in excellent agreement, provided p is not too small. We must look elsewhere to solve the mystery.

When we estimated v_b as a bound for v starting from Eq. 15, we explicitly stated that we were using a sufficient condition for the candidate unstable void, i.e., that this had to be a square all throughout the sequence. However, this is not a necessary condition. In principle, even if the void cannot grow conserving its aspect ratio at some particular stage, it may still grow as a rectangle

and eventually become unstable later in the process, although this event cannot be accounted for when we estimate v_b from Eq. 15. In Fig. 2, we have an example of a configuration that for the modified model would lead the square process to stop before the largest is vacated entirely, while the same configuration would lead to an empty final state if we allow one small elongation. One can also prove that growth by rectangular voids of different sizes and elongations encompasses (i.e., exhausts) all self-efficient transformations through which a nucleating center can engulf one by one, neighbor by neighbor, the particles in the entire lattice. In other words, if a growing void cannot wipe out all particles in the system via rectangular transformations, it cannot do so on its own in any other way. The condition of growth by rectangles is not only a sufficient one (as it was in the case of squares) but also necessary. Consequently a calculation (if available) of the type derived in Eq. 15, but dealing with rectangles instead of squares as the intermediate transition states, would gain us access to v exactly.

For the modified model in $d = 2$ this is exactly what can be done (De Gregorio et al. 2005). Instead of using Eq. 15 to estimate v_b , one can generalize the method and determine v accurately for any density, without the need to simulate the model. The procedure entails mapping the growth by rectangles into an explicit form that takes the form,

$$P_{m,n}^i = \sum_j \left(c_{m,n}^{ij} P_{m-1,n}^j + d_{m,n}^{ij} P_{m,n-1}^j \right) \quad (19)$$

In Eq. 19, $P_{m,n}^i = P_{m,n}^i(p)$ represents the probability that the nucleation process via rectangular growth will be found after $m + n$ steps to occupy the state i . The state i at given m, n is typically a rectangle of sides $m \times n$ that is entirely empty but eventually for some of the lines on its contour that may be entirely occupied (which ones these are is in fact characteristic of the label i itself). The range of i 's and of j 's coincide. The map is constructed purposefully in such a way that the transitions from state to state can be expressed in the linear form Eq. 19. Concurrently, it has to be constructed so that the transitions coefficients $c_{m,n}^{ij} = c_{m,n}^{ij}(p)$

and $d_{m,n}^{ij} = d_{m,n}^{ij}(p)$ have explicit expressions (which are similar but not equal to the partial terms employed in the product Eq. 15 for squares). The mapping is not unique, as in the end we are going to take the limit $m, n \rightarrow \infty$, but any map in the form (Eq. 19) has to satisfy the two conditions above. From the set of states with probabilities $P_{m,n}^i$ there must be one, say $i = 1$, for example, that represents an $m \times n$ rectangle completely empty. $P_{m,m}^1$ is therefore the probability for an empty square to arise after $2m$ steps, and v will equal $v = \lim_{m \rightarrow \infty} P_{m,m}^1$. The map in Eq. 19 can be easily solved numerically. $P_{m,m}^1$ converges sufficiently rapidly to v so that we can genuinely calculate numerically v for almost any value of p , well beyond anything of physical interest.

By solving Eq. 19, we therefore have the exact v for any particle density p for the $d = 2$ modified model. Agreement with its value from computer simulations is beyond the most optimistic expectations (De Gregorio et al. 2005). From $v \simeq 1/L_c^2$, we now have a reliable interpolation to the bootstrap critical length for any system size that is available from computer simulations, plus a prediction for v and therefore L_c well beyond scales of even physical interest, let alone one-day-to-be computational limits. This procedure lacks the insight and elegance of compact formulas such as the one in Eq. 4, but it has the merit (at least for two-dimensional models) to wash away all uncertainties related to previously irreconcilable mathematical and computational differences.

Once we have v for any p , we can access many quantities that are normally available only via computer simulation, with the advantage that now we do not have any important limitation in regard to system sizes. Thus, for example, we may infer, approximately, the probability that a spanning cluster survives the culling process, given the system size L and the particle density p . We have

$$P_{CI}(p, L) \simeq \Theta(1 - L^2 v(p)) [1 - L^2 v(p)] \quad (20)$$

meaning that the average probability $1 - P_{CI}$ that a cluster does not survive the culling process is proportional to the average number of connected holes for that size. In essence, a reelaboration of

our (in)famous $L^2 v \simeq 1$. The prefactor with the Θ step function (equal to 0 if its argument is negative and to 1 if positive) guarantees that P_{CI} is positive definite. In Fig. 1, we have P_{CI} as a function of p for four different system sizes. We have already appreciated the same figure in a previous explanatory section, and to whoever may have wondered how one could have those largest system sizes from computer simulations the trick is now revealed.

We may also try to fit $L_c \simeq 1/\sqrt{v}$ using the expression given in Eq. 13. In essence, we thus try to infer the form of $f(q)$. Although this is only a best fit, and has no rigorous analytical basis, it is suggestive, because we can access virtually any large value of L_c from the knowledge of v (even up to 10 to the order hundred). It is also insightful because it gives a flavor of the magnitude of the correction. An excellent fit at $q \ll 1$ bears (De Gregorio et al. 2006), for example, $f(q)$ in the form $f(q) \approx -Bq^{-\beta}$, where B is a fitting constant of a few units, and the best estimate for β is $\beta \approx 2/3$. The modulating prefactor in Eq. 13 given by $\exp[f(q)]$ is therefore moderating the divergence of the asymptotic contribution. From Eq. 12, one sees that by successive iterations one can get $\epsilon(L)$ (which is negative as $f(q)$ is negative), but in general the form in Eq. 4 is less convenient (and less natural) than the one in Eq. 13. More explicitly, we have that if $qf(q) \ll 1$ and $f(q) \approx -Bq^{-\beta}$ hold, we estimate $\epsilon(L) \approx -C/(\ln L)^{1-\beta}$ for diverging L , where C is a constant. Gravner and Holroyd first proved (Gravner and Holroyd 2008) that $\epsilon(L)$ indeed must approach zero no faster than $-\text{Const}/\sqrt{\ln L}$. This implies $\beta > 1/2$. Later they introduced a process called local bootstrap percolation (Gravner and Holroyd 2009), a three-state rather than two-state irreversible process with at most one single nucleation process, and for which Equation 19 would yield an exact probability of success. For this variant they proved also an upper bound of $1/2$, which is less than the extrapolated value of $2/3$ above. The striking conclusion is that not even the rigorous correction term can be captured reliably by the numerical exact solution yet, when the probability of success becomes as small as 10 to the negative few hundreds. The results in Gravner and

Holroyd (2008, 2009) use rectangular processes rather than square processes and have been later framed in slightly more generality in (Bringmann and Mahlburg 2012).

Bethe Lattice Calculations: The Cases $m \geq 2$

As we have seen in the previous sections, we are always able to classify the behavior of bootstrap percolation model if either $m < 2$ i.e., $k \leq 2$) or, for regular lattices, if $m \geq d$ (i.e., $k > d$). The former cases fall under the same universality classes of standard percolation and are valid for any lattice geometry and any dimension. The transition is continuous and characterized by universal exponents (Branco 1993; Chaves and Koiller 1995; Medeiros and Chaves 1997). The latter class is that with a critical concentration p_c that is unity for an infinitely extended system and is more reminiscent of first-order transition behavior. It is characterized by the absence of any genuine power-law behavior in the relevant quantities. Notice also that, for regular lattices, $d = z/2$. If we then generalize the condition $m \geq d$ to the condition $m \geq z/2$, we are allowed to include the triangular lattice (Kogut and Leath 1981) in the same class discussed in the two previous sections, as well as the face centered cubic lattice (fcc), as simulation results suggest (Lawlor et al. 2005) (it would be interesting to determine rigorously whether $m \geq z/2$ is a general requirement for belonging to the second class of models for any lattice geometry). A question arises as to whether, depending on the lattice geometry and the dimensionality, there can be other classes with behavior different from the two classes above. The rationale for this expectation has three motivations. First is the obvious observation that there are dimensions and lattice geometries for which some values of the parameter m are not covered by either class, and we cannot apply the general theoretical frameworks of above. Examples are the fcc lattice with $m = 2, 3, 4, 5$ ($k = 3, 4, 5, 6$) or the $d = 4$ hypercube lattice with $m = 2, 3$ ($k = 3, 4$). A second motivation is that as we admit conditions for

culling that include an extended neighborhood larger than the set of nearest neighbors, different classes of behavior do appear to arise (Schwarz et al. 2006; Toninelli et al. 2006). The third motivation stems from the earliest results that were obtained within bootstrap percolation calculations on Bethe lattices (Chalupa et al. 1979), which were unexpected in nature as will be discussed briefly. The Bethe lattices are graphs with no closed loops and therefore many geometric specific correlations associated to Euclidean lattices are washed away. On the other hand, they are often regarded as mean-field models for the associated transitions (in this case the bootstrap transitions). In this sense, they might be seen as characteristic of genuine bootstrap behavior in infinite dimensions. Depending on the lattice geometry and on the dimension, remnants of the ideal Bethe-like behavior might be observed.

In a Bethe lattice (or Cayley tree) with coordination number z , every site is linked to z other sites. In turn each one of those sites is linked to $z - 1$ other sites all disconnected with each other, and so on in a hierarchical fashion. As usual, each site is initially populated by particles with random probability p . The bootstrap percolation rule is unchanged, i.e., we assign a rule so that at each iteration occupied sites that have m or less occupied sites among the z neighboring are removed, while those with $k = m + 1$ or more that are occupied remain occupied. After many iterations we check for the presence of a spanning cluster formed by the remaining particles. For $m = 0$, only isolated sites are removed, and we have as usual standard nearest neighbor percolation on the Bethe lattice, with a critical concentration $p_c = 1/(z - 1)$ and a probability $P_\infty(p)$ that a site is occupied by a particle belonging to the spanning cluster that vanishes linearly in $p - p_c$, when p approaches p_c from above. Also for the case $m = 1$ $P_\infty(p)$ vanishes at p_c , but this time with a nonuniversal exponent of 2 (Chalupa et al. 1979). Naturally, the case $m = z - 1$ ($k = z$) is trivial, because for any $p < 1$ all particles can be removed one after the other. The most interesting case is when $2 \leq m < z - 1$ ($2 < k \leq z - 1$). One finds that for any given p the probability $P_\infty(p)$ that a site hosts a particle belonging to the infinite k -cluster is given by,

$$P_\infty(p) = 0 \quad p < p_c$$

$$\simeq a + b(p - p_c)^{\frac{1}{2}}, \quad p \geq p_c, p \simeq p_c \quad (21)$$

We have therefore a discontinuity at p_c , and concurrently the order parameter has critical behavior when $p \rightarrow p_c^+$. Noticeably, $\partial P_\infty / \partial p \simeq (p - p_c)^{-1/2}$ when p approaches p_c from above. Furthermore, a correlation length diverging at p_c (identified as the susceptibility) has been found to exist (Schwarz et al. 2006), thus showing that the transition on the Bethe lattice for $m > 2$ is of a hybrid nature.

To proceed for the general case, we may define the probability R that a given site is *not* connected jointly with one specified neighbor to a k -cluster that may eventually span the system. This probability R must satisfy a condition of self-consistency of the type,

$$R = 1 - p$$

$$+ p \sum_{n=0}^{m-1} \binom{z-1}{n} R^{z-1-n} (1-R)^n \quad (22)$$

We also define $T = 1 - R$ and we can illustrate the result (Chalupa et al. 1979; Moukarzel et al. 1997; Sellitto et al. 2005) in Eq. 21 briefly for the case $z = 4$ and $m = 2$ as a concrete explanatory example. In this case, all the particles in the surviving spanning cluster must have three or more occupied neighbors. We can imagine a hierarchical organization of connected links in which three links from upward merge into one site that has one other link going downward and that will itself merge with two other links from sideways, and so on. $T (= 1 - R)$ is the probability that a site is connected to at least two among the three sites merging from above it, all of which are themselves connected to at least two of the three sites above, and so on indefinitely. If $T = 0$, we immediately conclude that there cannot be any spanning cluster with connectivity three. On the other hand, if $T > 0$, the opposite is true. This is not straightforward, but it suffices to realize that if a site is occupied, and if at least three of the four nearest neighbors are each part of the substructure defined by the probability T , it follows that particle

must necessarily belong to a spanning cluster of connectivity three. The probability T must satisfy the following relation of self-consistency,

$$T = p[T^3 + 3T^2(1 - T)] \quad (23)$$

which is equivalent to Eq. 22 above for $R = 1 - T$, while the probability that a site belongs to the spanning cluster is given by,

$$P_\infty = p[T^4 + 4T^3(1 - T)] \quad (24)$$

Equation 23 always admits the solution $T = 0$ for any p . We can eliminate T on both sides and seek for the solutions with $T \neq 0$. We must solve,

$$2T^2 - 3T + \frac{1}{p} = 0 \quad (25)$$

which has as a physical solution the only real root such that $T = 1$ when $p = 1$, which is

$$T = \frac{3}{4} + \sqrt{\frac{9}{16} - \frac{1}{2p}} \quad (26)$$

As we see, for any $p < 8/9$, T has no nonzero real solutions. It has the solution $T = 3/4$ when $p = p_c = 8/9$, which shows the discontinuity explicitly. We can write Eq. 26 in the convenient form,

$$T = \frac{3}{4} + \sqrt{\frac{p - p_c}{2pp_c}} \quad (27)$$

which takes the desired form, as $p \rightarrow p_c^+$,

$$T = \frac{3}{4} + \frac{1}{p_c \sqrt{2}} (p - p_c)^{\frac{1}{2}} \quad (28)$$

From the above expression for $p \rightarrow p_c^+$ combined with Eq. 24 we can easily verify that the relation (Eq. 21) holds for $z = 4$ and $m = 2$.

Probabilistic Bootstrap Percolation

Regular lattices have the disadvantage that the coordination number z is relatively small, and we do not have a very wide spectrum of choices

for the parameter m . One way to circumvent this problem in planar lattices is to extend the neighborhood of influence of a given site, so as to artificially enlarge the formal coordination number at each site. In this way, the bootstrap rule for removal of one particle is set to depend on the state (occupied or vacant) of many sites, beyond the mere nearest neighbors. Mixed transitions arise in these cases (Schwarz et al. 2006; Toninelli et al. 2006), although not exactly expressible in a form quantitatively identical to that given in Eq. 21.

Another approach that was taken by Branco (1993) was to introduce a probabilistic bootstrap model. This involves a simple extension to the model by considering mixtures of particles with different bootstrap rules. The particles are again occupied with density p , but each particle is assigned its own threshold m_i as a criterion for removal during the bootstrap procedure. Branco (1993) studied the case of a simple mixture of two types: m or m' with probability r and $1 - r$, respectively. The motivation is to study noninteger values of m by controlling the mixing parameter r . The model is exactly solved, and the results show that we can recover the full range of behavior from a continuous transition ($\beta = 1$) to the standard discontinuous or hybrid transition ($\beta = 1/2$).

The interesting cases are the ones which interpolate between continuous $m < 3$ and discontinuous transitions $m' \geq 3$ for the simple cubic lattice.

Using mixtures of particles with different rules is a promising approach for investigating the nature of bootstrap transition on real lattices (Lawlor et al. 2008) in two and three dimensions where simple nearest-neighbor models do not conclusively show the hybrid transition of Eq. 21.

Another case that has been studied is the $m = 2$ case on the square lattice in a polluted environment (Gravner and McDonald 1997), i.e., in the presence of a random fraction s of sites that are neither occupied nor empty. The occupied sites can be removed only if at least two neighboring sites are empty, and thus polluted sites may sometimes obstruct the culling process. It is found that even at low pollution s , if additionally $q < \sqrt{s}$,

then with finite probability many particles survive the bootstrap process, no matter how large the system.

The general result in Eq. 21 is suggestive also for other reasons. An identical relation (with the same exponent) to that of Eq. 21 holds if we replace P_∞ with the average number of touching hard spheres in the proximity of the jamming transition, at a given packing fraction (O'Hern et al. 2003). Similar correspondences can be made with other quantities, still bearing the same exponents. It has been natural to investigate whether similar hybrid transitions as shown in the Bethe lattice survive if we pass from the loopless case back to bootstrap percolation on Euclidean lattices. Undoubtedly this cannot be true in general, for Eq. 21 is valid for any z and for any $m \geq 2$, while we know already from the previous sections that Eq. 21 does not hold for the square lattice when $m = 2$ and for the simple cubic lattice in the case $m = 3$. Furthermore, when very large system sizes are tested, it appears that also for the case $m = 2$ for the simple cubic lattice all exponents lie in the same universality classes of standard percolation (Branco and Silva 1999) (i.e., of continuous phase transitions). The former case ($m = 2$ simple cubic) is particularly interesting. The critical concentration is estimated to lie in the vicinity of $p_c \simeq 0.573$, higher than that of the standard $m = 0$ and $m = 1$ value of $p_c \simeq 0.312$. All exponents but the exponent β (related to the vanishing of P_∞) were recognized to be universal (Adler and Stauffer 1990; Kogut and Leath 1981). Later, results for sizes larger than tested before suggested that also β might be universal (Branco and Silva 1999). Therefore we conclude that we must rule out all nearest-neighbor bootstrap percolation models on regular lattices in $d = 2, 3$ (square and simple cubic), if we want to recover the behavior as shown in Eq. 21.

High-Dimensional Lattices

Another scenario that we can envisage involves high-dimensional Euclidean lattices. It has been shown that high dimensionality expansions of the infinite dimensional Bethe lattice calculations, by

means of perturbative methods (Harris and Schwarz 2005), produce results that are qualitatively similar to Eq. 21 at sufficiently large d . In other words, for $m \geq 2$ and for high d we might encounter hybrid mixed transitions also for regular Euclidean lattices. This result has been somewhat complemented by the work of Balogh et al. (2007) for $m = d$ on hypercubic lattices as discussed towards the end of section “Void Instability and Rigorous Results,” whereby if d grows with L at a certain (slow) rate $d(L)$, we find $p_c = 1/2$, in contrast to $p_c = 1$ which is found for fixed d (a matter of future investigations will certainly be to determine whether p_c drops from 1 to $1/2$ discontinuously for different $d(L)$). Whether such hybrid transitions can be observed in high d geometries is a matter of present investigations. Simulations in the $d = 4$ hypercubic lattice with $m = 3$ seem to suggest (Parisi and Rizzo 2006) that a discontinuity does arise at p_c , but that this is not associated with a diverging susceptibility (which is always finite at the transition). This is a reflection of the fact that the putative critical point appears to be at a concentration lower than p_c . Thus the discontinuous jump at p_c would be purely first-order in nature.

k -Core Percolation on Random Networks

The bootstrap percolation problem has been studied on random networks, where it is commonly known as k -core percolation. The k -core is the largest connected cluster of the network (occupation density p) in which all the nodes have at least k neighbors, each of which is also in the subgraph. The k -core is found by removing all nodes with less than k neighbors – this culling process is repeated until all remaining nodes (if there are any) have at least k neighbors. The k -core extends the simpler notion of the giant connected component of a network and provides a useful description of a network in terms of successively nested cores. The first exact solutions of this problem were obtained by Chalupa et al. (1979) on the Bethe lattice (an infinite regular graph) as detailed above in Eq. 21. After some progress was made in determining thresholds for

the emergence of a k -core in random networks (Balogh and Pittel 2007; Fernholz and Ramachandran 2003; Pittel et al. 1996), an exact solution was recently described by Dorogovtsev et al. (2006) for uncorrelated, damaged or undamaged random networks with an arbitrary degree distribution.

We give a brief outline of the solution here. The starting point is the configuration model (Bollobás 2001; Newman 2003), an uncorrelated random network with a given degree distribution. An important point about this model is that the probability of there being more than one path between any pair of nodes is $O(n^{-1})$ where n is the number of nodes, and so the local structure of the network is tree-like. Making use of the tree-like structure of the network it is observed that the k -core coincides with the infinite $(k - 1)$ -ary subtree (in a k -ary subtree each node has at least k neighbors). We can therefore be certain that a randomly chosen node belongs to the k -core if at least k of its neighbors are the roots of $(k - 1)$ -ary subtrees. This quantity, which we call R , is the probability that a randomly chosen node is *not* the root of a $(k - 1)$ -ary subtree. As R is defined it only describes one end of an edge and is independent of whether the other end is in the k -core or not. If we choose an edge at random from the network, then it belongs to the k -core if both ends are the roots of $(k - 1)$ -ary subtrees and so with a factor of $(1 - R)$ for each end of the edge we can express R in terms of the number of edges in the k -core, L_k

$$\frac{L_k}{L} = (1 - R)^2 \quad (29)$$

The parameter R plays the role of the order parameter in k -core percolation and this expression relates it to simple measurable quantities of the networks (statistics of edges in the k -core).

Another basic quantity of interest is the relative size of the k -core M_k :

$$M_k = p \sum_{n \geq k} \sum_{q \geq n} P(q) C_n^q R^{q-n} (1 - R)^n \quad (30)$$

In this expression, $C_n^q R^{q-n} (1 - R)^n$ is the probability that exactly n neighbors are roots and $q - n$

are not roots of $(k - 1)$ -ary trees (where C_n^q is the binomial coefficient) and $P(q)$ is the probability that a node has q neighbors.

The nodes that comprise the k -core itself constitute an uncorrelated network and so their structure is encoded in the degree distribution of the k -core $P_k(n)$ (the probability that a node in the k -core has n neighbors):

$$P_k(n) = \frac{M_k(n)}{M_k} \quad (31)$$

Order Parameter for k -Core Percolation

In general, to find the physical quantities of interest, we must first solve for R for a given state of the network (R depends on k and the damage p). A given end of an edge is the root of a $(k - 1)$ -ary subtree (with probability $(1 - R)$), if at least $(k - 1)$ of its children are also the roots of $(k - 1)$ -ary subtrees. The exact expression is (Goltsev et al. 2006):

$$1 - R = p \sum_{n=k-1}^{\infty} \left[\sum_{i=n}^{\infty} \frac{(i+1)P(i+1)}{z_1} C_n^i R^{i-n} (1-R)^n \right] \quad (32)$$

where z_1 is the first moment of the degree distribution, and $(i+1)P(i+1)/z_1$ is the number of

out edges of the node arrived at from a given edge. This equation bears some similarity to that for ordinary ($k = 2$) percolation (see, for example, Eq. 1 of Chalupa et al. (1979)). As in $k = 2$ percolation, it is found that there are two possible solutions: $R = 1$: leading to a continuous transition, and $0 \leq R < 1$: leading to a discontinuous/hybrid transition. The critical behavior for the $R < 1$ case is found to be (Dorogovtsev et al. 2006; Goltsev et al. 2006):

$$R^* - R \propto (p - p_c)^{1/2} \quad (33)$$

where R^* is the value of order parameter at the point where the k -core vanishes. This hybrid critical behavior, characterized by a jump in the order parameter at $p_c < 1$ and a square root singularity in the percolating phase, is shared by other quantities, such as the relative size of the k -core, M_k :

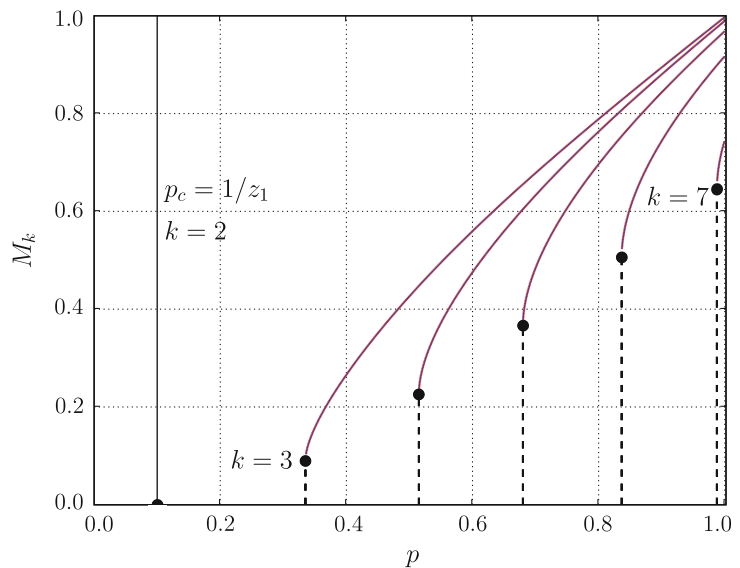
$$M_k - M_k^* \propto (p - p_c)^{1/2} \quad (34)$$

As the bootstrap process removes nodes at random, the cores are destroyed starting with the highest k -core. Each k -core collapses with the critical behavior of Eq. 33.

In Fig. 4, we show the relative sizes of all the possible k -cores in networks with Poisson degree

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Fig. 4 The relative size of the k -core for a classical Erdős-Renyi random network. The mean degree $z_1 = 10$. The case $k = 2$ corresponds to ordinary percolation where there is a continuous transition at $p_c = 1/z_1$. For $3 \leq k \leq 7$, we see that a core emerges with a discontinuous jump in M_k (see Eq. 34)



distributions ($z_1 = 10$) as a function of occupation density.

These results hold for networks with arbitrary degree distribution but z_2 must also be finite. In scale-free networks (degree distribution $P(q) \propto 1/(q+c)^{-\gamma}$) with $\gamma > 3$, where z_2 is finite, the critical behavior for $k \geq 3$ -core percolation is found to be the hybrid phase transition (Eq. 33). For $2 < \gamma \leq 3$ the transition is infinite order, similar to the case for ordinary percolation in scale-free networks.

It is worth noting that the hybrid transition indicates there should be a diverging length-scale which has not been conclusively identified – it is the mean size of finite clusters which drives the conventional continuous transition, but for tree-like network models it is not obvious what the nature of divergence is since finite clusters are not supported for $p < p_c$.

The first clues to understanding the nature of the hybrid transition were found by studying the critical behavior of the subset of the k -core known as the corona (Schwarz et al. 2006). The corona is comprised of nodes in the k -core which have exactly k neighbors in the k -core (this is the minimum number they can have). The nodes in the corona are randomly distributed throughout the k -core and for $p > p_c$ the corona is comprised of small finite clusters. It is an important observation that if a random node in the k -core is removed, then all the nodes in the corona clusters attached to that original node will be removed, leading to increasingly massive cascading removals, contingent on the removal of a single node, on approach to the transition.

The precise behavior of the mean size of clusters in the corona attached to a randomly chosen vertex in the k -core, N_{crn} , is known for random networks (Dorogovtsev et al. 2006; Goltsev et al. 2006). It diverges at the transition,

$$N_{crn} \propto (p - p_c)^{-1/2} \quad (35)$$

as was also found by Schwarz et al. (2006) for the Bethe lattice. The picture that emerges is one of the collapses of the k -core at p_c , accompanied by a percolation transition of the corona cluster. For $p > p_c$ the corona clusters are disconnected,

while for $p < p_c$ there is neither a k -core nor any corona clusters. As in ordinary percolation, we can identify a susceptibility belonging to the mean size of the clusters in the corona. Goltsev et al. (2006) find that this susceptibility diverges also at the transition, indicating that the corona clusters undergo a percolation transition, growing in size as $p \rightarrow p_c^{(+)}$, percolating at $p = p_c$, and disappearing altogether for $p < p_c$.

There have been some attempts to apply the above picture of k -core percolation to real networks, such as the Internet (at the Autonomous System level) (Alvarez-Hamelin et al. 2005). The identification of the k -cores provides a useful insight into the structural properties and regions of increasing centrality in these networks. Although the results are promising, they are not in precise agreement with the predictions, a consequence of the fact that the theory deals only with uncorrelated networks.

Future Directions

Future work will continue to try to understand the unusual scaling behavior and further develop rigorous results. The existence and the consequent classification of the transitions described above, including but not limited to hybrid mixed transitions, is likely to represent the next step for many working on bootstrap percolation transitions. The development of solutions for complex networks, k -core percolation, will lead to many new directions of interest including an understanding of the effect of correlations and loops. The broad range of applications that the bootstrap percolation problem has already found will continue to inspire fruitful research in diverse areas of physics and mathematics.

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Invasion Percolation

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Article Outline

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Glossary

B	Bond number
D_b	Backbone
D_f	Fractal dimension
D_{min}	Fractal dimension of minimum path
fBm	Fractional Brownian motion
fLm	Fractional Lévy motion
H	Hurst exponent
IP	Invasion percolation
NTIP	Non-trapping invasion percolation
OP	Ordinary percolation
p_c	Ordinary percolation threshold
S_r	Residual saturation
TIP	IP with trapping
ξ_w	Correlation length
ν	Percolation correlation length exponent
ϕ	Porosity
g	Field gradient
Z	Coordination number
a	Standard deviation

Terms

Defender	Fluid initially within pore space.
Invader	Second fluid injected to displace defending fluid (defender).
Drainage	Displacement of a wetting fluid by a non-wetting fluid.

Definition of the Subject

Invasion percolation is a simple dynamic process describing the slow displacement of one fluid by another in a porous material. This is a common phenomena with many important applications; these include the penetration of nonaqueous polluting liquids into soil, the penetration of air into porous media such as soil, concrete, wood and ceramic powder during drying and the displacement of water from soil and rocks by gases generated by buried waste. A final important example, which is the primary focus of this review, is the accumulation during initial migration and the subsequent recovery and production of hydrocarbon reservoirs. Experiments on idealized systems have shown that the simple invasion percolation model provides a very realistic description of the slow fluid-fluid displacement processes associated with these important applications. Experiments and simulations of invasion percolation have been extended to consider the role of gravity, wettability and the complex nature of real porous materials on the dynamic immiscible displacement processes.

Introduction

Invasion percolation is a dynamic process that was proposed to describe the slow immiscible displacement of one fluid by another in a porous medium. Many porous media can be represented by a network of pores (sites) connected via throats (bonds) (Chandler et al. 1982; Lenormand and

Bories 1980; Wilkinson and Willemsen 1983). In this representation all the pores and throats are initially filled with *defending* fluid. When a second fluid is injected very slowly into the porous medium such that the capillary forces dominate the viscous forces, the dynamics is controlled by the size of the local pore or throat. In a drainage process (the displacement of a wetting fluid by a nonwetting fluid), capillary forces are strongest at the narrowest places in the medium; in the pore throats. A drainage process is therefore represented as a series of discrete jumps across throats in which the non-wetting fluid displaces the wetting fluid via the *largest throat* (offering the least resistance to displacement). This is the version of the model originally considered by Chandler et al. (1982), equivalent to bond invasion percolation. Wilkinson and Willemsen (1983), who were the first to use the term *invasion percolation*, considered the process of imbibition (a non-wetting fluid being displaced by a wetting fluid) at a constant but infinitesimal (capillary dominated) flow rate. In this scenario the capillary forces are again strong in the throats, so the wetting fluid invades the throat quickly, but slows when entering the larger pores. This motion can be described by a series of discrete jumps in which at each time step the wetting fluid advances through the *smallest available pore*. This is site invasion percolation. In the absence of trapping, the bond version can be reduced to the site version through bond to site transformations. However, when trapping is introduced where regions of defending fluid are incompressible and cannot escape, the transformation becomes a correlated site-bond problem (Wilkinson and Willemsen 1983).

Most implementations of invasion percolation have been on a regular lattice. Sites or bonds representing pores and throats are usually assigned uniformly distributed random numbers as it is the sequencing of the events that is important, independent of the distribution. For drainage, invasion percolation is generally considered to be a good model. Although Wilkinson and Willemsen (1983) used site invasion percolation for imbibition, later work by Blunt and Scher (1995) has this as a special case where different alternative modes of wetting invasion are possible.

Classical Definitions, Algorithms and Results

Invasion Versus Ordinary Percolation

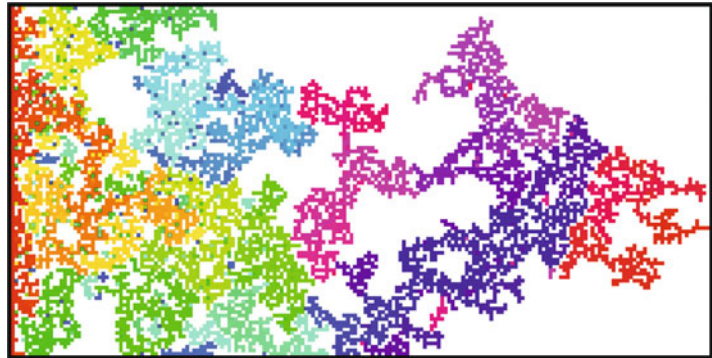
There are distinct differences between invasion percolation (IP) and ordinary percolation (OP). Invasion percolation starts with a well defined interface (inlet) and displaces the defending phase in a systematic way until spanning the system. In this way the concepts of history and the sequence of invading pores are naturally built into the model. The cluster generated in IP always spans a region between the injection face and the outlet face; there is no analogue to the percolation occupation probability p and there is only a single invasion cluster (no finite disconnected clusters). Figure 1 shows the spanning cluster at breakthrough of the invading phase for invasion percolation in two dimensions.

The implementation of trapping in the defending fluid introduces more differences. Monte-Carlo simulations of invasion percolation with trapping (TIP) in two dimensions (Wilkinson and Willemsen 1983) found that the fractal dimension of the sample spanning cluster was $D = 1.82$, significantly smaller than $D = 1.896$ for OP. Simulation of non-trapping IP (NTIP) gave similar values to OP. In three dimensions no significant difference in the IP and OP models was originally observed. The difference in the 2D values was assumed to be associated with trapping and the effect of trapping thought to be negligible in 3D. The question of the universality class of IP was not conclusively established at this time.

There was extensive experimental evidence in support of the IP model of two phase flow in porous media. Lenormand and Zarcone (1985) performed air drainage of oil in a transparent two-dimensional etched network of pores. Analysis of the fractal dimension of the invading phase gave $D = 1.82$ consistent with 2D simulations of TIP. In a further range of drainage experiments with a variety of wetting and non-wetting fluids including oil, air, water and different sucrose solutions Lenormand and Bories (1985) showed that the results were completely consistent with an IP description of the phenomena. Stokes et al. (1986) considered displacement patterns in a cell packed

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Fig. 1 Invasion percolation on 2D lattice. The invader (*colored*) enters from sites on the *left hand edge* and the defender exits from the *right hand edge*. Different colors indicate sites added within different time intervals



with unconsolidated glass beads. They found that under drainage conditions the resultant fluid displacement patterns were consistent with IP. Chen and Wada (1986) used a technique of index matching fluids to visualize the fluid distributions of a quartz bead pack; again the fluid distribution patterns are reminiscent of IP. While the main application of IP has been to the description of the evolution of the interface between two immiscible fluids, IP also has applications to other problems including the characterization of optimal paths and domain walls in strongly disordered media (Cieplak et al. 1994; Porto et al. 1997) minimum spanning trees (Dobrin and Duxbury 2001) and the simulation of the Ising model at the critical temperature (Franzese et al. 1998). Moreover, IP is one of the simplest parameter-free models which exhibits self-organized critically (Stark 1991).

Methods and Algorithms

An elegant and fast algorithm for invasion percolation can be found in the book by Richard Gaylord and Paul Wellin (1994), together with a detailed explanation. This algorithm, written in Mathematica, is included for convenience in Algorithms 1 and 2. As listed, this code starts on a square lattice with a single seed at 0,0 and maintains a list of potential invasion sites on the boundary as the cluster grows. It is straightforward to modify this algorithm to include boundaries and a different initial cluster.

Trapping IP results were for many years limited to small lattice sizes due to the time needed to search for the trapped regions at each time step. In the conventional algorithms the search for the

trapped regions was done after every invasion event using a Hoshen–Kopelman algorithm (Hoshen and Kopelman 1976; Stauffer and Aharony 1994), which traverses the whole lattice, labels all the connected regions, and then only those sites (bonds) that are connected to the outlet face are considered as potential invasion sites (bonds). A second sweep of the lattice is then done to determine which of the potential sites is to be invaded in the next time step. Thus each invasion event required $O(N^2)$ calculations and limited TIP simulations to small lattice sizes.

Sheppard et al. (1999) developed more efficient algorithms for generating TIP simulations. They noted, firstly, after each invasion event only a small local change is made in the interface; implementing the global Hoshen–Kopelman search is unnecessary. Secondly, it is wasteful to traverse the entire lattice at each time step to find the most favorable site (bond) on the interface since the interface is largely static. The first problem is tackled by searching the neighbors of each newly invaded site (bond) to check for trapping. This is ruled out in almost all instances. If trapping is possible, then several simultaneous breadth first “forest-fire” searches are used to update the cluster labeling as necessary (Babalievski 1998). This restricts the changes to the most local region possible. Since each site (bond) can be invaded or trapped at most once during an invasion, this part of the algorithm scales as $O(N)$. The second problem (identifying the sites for invasion) was solved by storing the sites (bonds) on the fluid-fluid interface in a list, sorted according to the capillary pressure threshold (or size) needed to invade them. This list is implemented via a balanced

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Algorithm 1 Mathematica algorithm for generating invasion percolation clusters from a single starting cell. Code is from (Gaylord and Wellin 1994). In Mathematica version 6 `Table[Random[],{4}]` can be replaced with `RandomReal[{0,1},4]`

```
Invasion[n_Integer]:=
Module[{pickAndChoose, nn, newnn, newpers, newPerLis,
  choices = {{1,0}, {0,1}, {-1,0}, {0,-1}}},
  pickAndChoose :=
    (newcluSite = Sort#[[2]][[1, 2]];
     nn = Map[Function[y, y + newcluSite], choices];
     newnn = Complement[nn, #[[1]],
       Transpose#[[2]][[2]]];
     newpers = Transpose[{Table[Random[],
       {Length[newnn]}],
       newnn}];
     newPerLis = Join[DeleteCases#[[2]],
       {_, newcluSite}], newpers];
  {Join#[[1]], {newcluSite}}, newPerLis})&;

Nest[pickAndChoose,
  {{{0,0}}, Transpose[{Table[Random[], {4}],
    choices}]},
  n][[1]]
]
```

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Algorithm 2 Mathematica code that can be used to plot clusters generated from the `invasion[]` function

```
ShowSpread[list_, opts___]:= Show[Graphics[
  {Hue[0.77],
   Map[{Rectangle[#-{0.5,0.5}, #+{0.5,0.5}]&, list]}
 ],
 opts, AspectRatio -> 1,
 PlotRange -> Map[{Min[#],Max[#]}&,Transpose[list]]]

ShowSpread[ Invasion[500] ]
```

binary search tree, so that insertion and deletion operations on the list can be performed in $\log(n)$ time, where n is the list size. The sites (bonds) that are designated as trapped using the procedures described above are removed from the invasion list. Each site (bond) is added and removed from the interface list at most once, limiting the cost of this part of the algorithm to $O[N \log(n)]$. Thus, the execution time for N sites (bonds) is dominated (for large N) by list manipulation and scales at most as $O[N \log(N)]$. This allowed multiple simulations of TIP at scales of 4000^2 in 2D and 500^3 in 3D.

Universality Class of TIP

TIP describes waterflooding processes in secondary oil recovery. If differences in the topology of the transport pathways for the bond based TIP

(drainage) and site-based TIP (imbibition) exist, this has a profound effect on the conductivity of the invading phase at the breakthrough point where a sample spanning cluster first forms (water breaks through during recovery). Differences have been noted in experimental measurements on rocks under different wettability conditions. Probing this question required simulating TIP processes on very large lattices. This allows one to obtain precise estimates for the fractal dimensions of the sample spanning cluster, backbone and minimal path.

In two dimensions it was found that these fractal dimensions are non-universal and vary with the coordination number Z of the lattices (Sheppard et al. 1999). The fractal dimension of the sample spanning cluster (SSC) of lattices with low Z exhibited the standard value of $D_f = 1.82$,

the fractal dimension crosses over to the value given by OP for large Z (>6). Values for the triangular lattice ($Z = 6$) seemed to give an intermediate value close to the prediction for OP. The same trends were seen with the value of the backbone and minimal path dimensions (Table 1). These results showed that the scaling properties of TIP in 2D are lattice dependent and hence non-universal.

It was initially thought that site- and bond-based IP were identical; results on large lattices showed distinct differences in the scaling properties of site-based and bond-based TIP. Results in 3D showed that site and bond TIP were in two distinct universality classes (Sheppard et al. 1999). Site TIP had the same scaling behavior as NTIP and OP. A second universality class was observed for bond TIP.

Overall the results show that while ordinary percolation, a static process, is described by a unique universality class, TIP, a dynamic phenomena does not possess a unique universality class. The difference in the topology of site-based and bond-based TIP can assist in the interpretation of experimental measurements of waterflooded rock under different wettability conditions; for an oil wet rock the conductivity of the water channels can be several orders of magnitude

smaller at breakthrough than for a comparable water wet rock; this difference is consistent with the different topology of the flow paths for site versus bond based TIP.

Trapping Thresholds for TIP

As the TIP cluster is a fractal at breakthrough, the initially spanning cluster has essentially zero density. However a percolation threshold can be defined for TIP; this occurs beyond the percolation point, and is associated with the disconnection of the defending phase. This second percolation threshold is reached when the defender phase no longer percolates through the system and consists only of isolated clusters. At this point the TIP process ends. In two dimensions this second threshold corresponds to the invading phase breaking through. In three dimensions the trapping does not occur until the invader has occupied a significant fraction of the pore space. In a porous rock with two immiscible fluids this second threshold is associated with the residual saturation of the defending phase; no more defending fluid can be displaced from the sample without increasing the flow rate and introducing viscous forces into the displacement process. The value of the threshold is therefore of important practical interest. Numerical estimates of the trapping threshold for TIP on a cubic lattice were given by Wilkinson and Willemsen (1983) as 0.66. Percolation and trapping thresholds have been related to the mean coordination number of the lattice (Heiba et al. 1992). Simulations of ordinary percolation on a range of simple lattices has led to the approximate relationships that $p_c^{\text{bond}} = 1.5/Z$ and $p_c^{\text{site}} = 2/z$ (Sahimi 1994). Galam and Mauger (1996) expanded on this idea and proposed a universal formula which in 3D is given by $p_c = p_0 (Z - 1)^{-a}$ where p_0 and a are constants which depend on the type of percolation considered. Percolation threshold for OP and OP with trapping followed this relationship (Paterson 1998). In a set of simulations on lattices of varying coordination number it was shown that the formula of Galam and Mauger (1996) matches the TIP threshold of the lattices with $Z > 6$. However values of the threshold for coordination numbers $Z < 5$ (Paterson et al. 2002) diverged from the

Invasion Percolation, Table 1 The most accurate estimates of various fractal dimensions for IP in 2D and 3D, and their comparison with those of random percolation (OP) (Sahimi 1994)

Model	D_f	$D_{\min}$	D_b
2D			
NTIP	1.8959	1.1293	1.6422
Site TIP ($Z < 6$)	1.825	1.203	1.217
Site TIP ($Z = 6$)	1.890	1.132	1.616
Site TIP ($Z > 6$)	1.895	1.136	1.642
Bond TIP ($Z < 6$)	1.822	1.214	1.214
Bond TIP ($Z = 6$)	1.823	1.215	1.215
Bond TIP ($Z > 6$)	1.895	1.221	1.221
OP	1.895	1.1307	1.6432
3D			
Site NTIP	2.524	1.3697	1.868
Site TIP	2.524	1.3697	1.861
Bond TIP	2.524	1.458	1.458
OP	2.524	1.374	1.87

prediction of Galam and Mauger (1996). The results are significant because of the application to the prediction of residual phase saturations in multiphase flow through porous media.

Modifications to Invasion Percolation

The invasion percolation model was originally developed to model two-phase displacements in porous media, with obvious application to oil recovery. However, even the early researchers in the field were aware that to be of practical significance and have utility the invasion percolation model would need to be extended to include gravity, viscosity, and other effects.

Introduction of Gravity

Gravity was first introduced into the invasion percolation algorithm by Wilkinson (1984) through the application of a simple linear weighting on the invasion thresholds in the direction of buoyancy.

An important application of invasion percolation with buoyancy is to the secondary migration of oil. Secondary migration is the slow process occurring over geological timescales where oil migrates from the source rocks where it is formed into structural or stratigraphic traps. It is in these traps where oil is found and produced, so a knowledge of secondary migration can be a key input into oil exploration. Secondary migration is a very slow process dominated by capillary and buoyancy forces, so invasion percolation is well suited to modeling this process as viscous forces can be safely ignored.

In a series of papers, researchers at the University of Oslo have explored invasion percolation as a model for secondary migration (Meakin et al. 1995, 2000; Vedvik et al. 1998; Wagner et al. 1997a, b). In particular they have studied the structure formed when the non-wetting fluid disintegrated into fragments (Meakin et al. 1992). They performed extensive two- and three-dimensional computer simulations and found that with a destabilizing external field on invasion percolation that displacement patterns were dominated by the growth of a single branch. This

branch could be described in terms of a connected string of blobs of size ξ_w , which form a directed random walk along the direction of the field. On length scales smaller than ξ_w , the displacement patterns had the structure of invasion percolation clusters without a destabilizing field. They found that dependence of the correlation length ξ_w on the magnitude of the field gradient g is given by $\xi_w \sim |g|^{-\nu/(\nu+1)}$ (where ν is the ordinary percolation correlation length exponent) in accord with the theoretical arguments of Wilkinson (1984, 1986).

A fundamental difference between invasion percolation and ordinary percolation is that invasion percolation generates a spanning cluster for lesser numbers of invaded sites, and this fraction of invaded sites tends toward zero as the network size increases. This is consistent with field observations; it can be very hard to detect secondary migration pathways that are only a thin filament occupying only an infinitesimal proportion of the exploration volume. Experiments conducted by Hirsch and Thompson on sandstone samples of different sizes found saturations consistent with these predictions from invasion percolation. Heterogeneity does however create local pools along the migration path, so there are occasions where parts of the path can be detected.

Pore-network simulations and concepts from invasion percolation in a gradient have been used to study the effect of gravity on the critical gas saturation in a porous medium. Critical gas saturation denotes the volume fraction of the gas phase at the onset of bulk gas flow during the depressurization of a supersaturated liquid in a porous medium. Tsimpanogiannis and Yortsos (2004) found that the critical gas saturation approaches two plateau values at low and high Bond numbers B . In the intermediate region it scales as a power law of B , which for a 2D lattice is $B^{-0.91}$.

Introduction of Viscous Forces

Invasion percolation corresponds to very slow displacements where viscous forces can be ignored. However, commercial extraction of oil is often at rates where viscous forces cannot be ignored hence there is incentive to expand the model to incorporate viscous forces. Wilkinson

(1984) was the first to suggest how percolation may be extended to include viscous forces through the use of a mean field description of the fluid flow. His ideas were developed further by Xu et al. (1998) in the limits of high and low viscosity ratios. For small viscosity ratios, they determined that displacement could be modeled by a form of gradient percolation in a stabilizing gradient, involving a particular percolation probability profile. In the opposite case, the displacement can be described by gradient percolation in a destabilizing gradient and this leads to capillary-viscous fingering.

Introduction of Wetting

Invasion percolation was originally formulated with very simple concepts of solid surfaces with uniformly wetting and non-wetting fluids. Wetting refers to the fluid that preferentially contacts the solid surface. Experiments in sedimentary rocks over time necessarily led to the development of models involving additional mechanism such as snap-off and film flow, extending basic invasion and ordinary percolation models (Blunt and Scher 1995). Further work on wettability showed that many rocks exhibit mixed-wettability, with the contact angle between the fluids varying with the diverse rock mineralogy (Blunt 1997). This has led to more complicated network flow models that increasingly depart from the simple original invasion percolation model (Blunt et al. 2002).

Effect of Pore Scale Structure on IP

In this section we consider the application of IP to the description of multiphase fluid flow in porous media at the pore scale. In order to produce realistic descriptions of the multiphase flow behavior of real porous materials requires one to obtain an accurate description of the morphology of the porous material. In this section we consider the importance of sizes and shapes of pores and throats and the presence of pore to throat correlations to IP. Equally important are the connection patterns of the pores and throats or the topology of the real porous network. Network topology is defined by parameters which include mean connectivity, coordination

number distributions and numbers of isolated clusters. In this section we describe the topological and geometric properties of a range of porous materials obtained from 3D images and compare them to classical lattices. Calculation of IP properties illustrates the importance of accurately reproducing the topology of real porous samples.

Measurement of Pore Scale Topology and Geometry

Direct Analysis of Pore Geometry and Topology Most studies of IP in 3D before 1995 were limited to regular cubic lattices. In recent years there has been mounting evidence that real rock topologies exhibit much lower coordination numbers. Ioannidis et al. (1997) measured the average coordination number $\bar{Z}$ from serial sections of a sandstone core and found $\bar{Z} = 4.1$. Bakke and Øren (1997), Øren et al. (1998) developed a process-based reconstruction procedure which incorporates grain size distribution and other petrographical data obtained from 2D thin sections to build network models that are analogues of real sandstones. The average coordination number $\bar{Z}$ of the resultant pore networks was significantly less than $Z = 6$. Recently, direct measurement of a 3D pore structure has become more readily available via synchrotron X-ray computed microtomography (micro-CT) (Dunsmuir et al. 1991; Flannery et al. 1987; Spanne et al. 1994), conventional micro X-ray CT (Arns et al. 2005) and laser confocal scanning microscopy (Fredrich et al. 1995). Coupled with skeletonization algorithms (Bakke and Øren 1997; Lindquist et al. 1996; Øren et al. 1998; Thovert et al. 1993) one can extract microstructural parameters for the direct input into network models. Lindquist et al. (2000) originally made measurement of the pore coordination number in equivalent network models derived from a suite of Fontainebleau sandstone samples with porosity varying from 7.5% to 22%. The average coordination number varied from $\bar{Z} = 3.37$ at $\phi = 7.5\%$ to $\bar{Z} = 3.75$ at $\phi = 22\%$. Moreover, the coordination number of the pores within each sample exhibited a broad distribution; the majority of pores were 3-connected, however some pores with $Z > 20$ were observed.

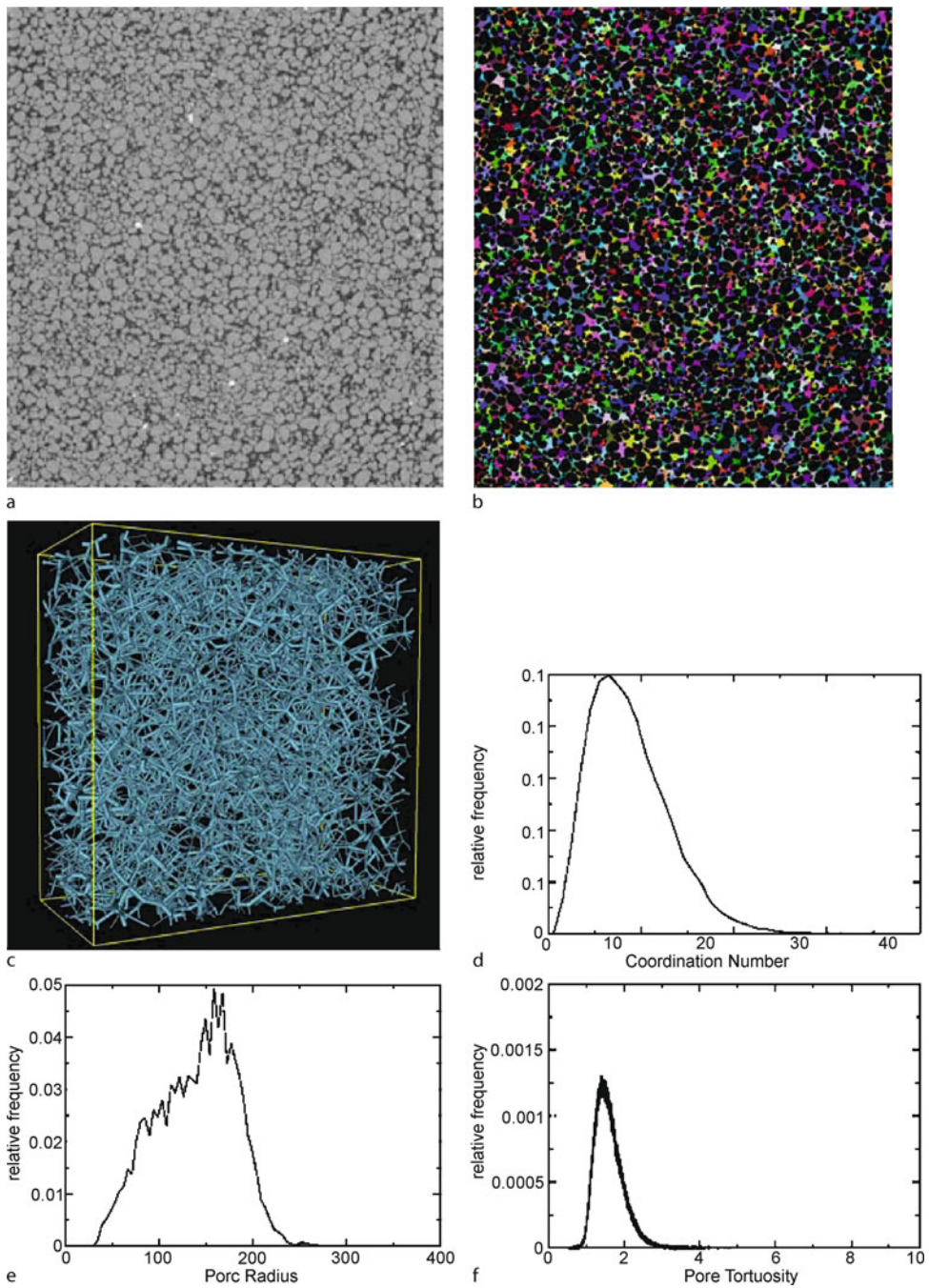
Extensive topological analysis of rock core material (Sheppard et al. 2005) from a range of geological settings (sandstones, carbonates) has shown that the mean coordination number Z is usually $Z < 6$. In Fig. 2a–c we show a slice of a sand pack, the partitioning of the subvolumes into over 300,000 individual pores and throats and the resultant pore network structure. The coordination number of the pore space is found to be $Z = 5.4$. The full coordination number distribution is shown in Fig. 2d. Some pores exhibit coordination numbers > 20 . From the partitioning one can also directly define the pore size, throat or constriction size, shapes and tortuosity of the pore structure in 3D. Examples of distributions of these properties are given in Fig. 2e–f.

In Fig. 3 and Table 2 we illustrate and quantify the pore structure and resultant pore topologies of three other granular systems and rocks. The samples include a consolidated sandstone, an idealized multiscale material and an outcrop limestone. In Fig. 3 we show the images of network subsets. The networks in Fig. 3 contain a small subset ($< 10\%$) of the full image volume obtained from the tomogram. However the information obtained is very rich in detail. The difference in the network structure for these four samples is visually dramatic. The more complex samples (bidisperse and limestone) can exhibit pores of extremely high coordination ($Z > 100$) and large volume weighted coordination numbers $Z > 30$ reflecting the high connectivity of the larger pores. Clearly the use of a simple cubic lattice gives a poor topological description of these systems.

Implication of Pore Topology to IP Properties As discussed in section “Trapping Thresholds for TIPS12”, percolation and trapping thresholds have been related to the mean coordination number of the lattice (Heiba et al. 1992). Simulations of ordinary percolation on a range of simple lattices has led to the approximate relationships that $p_c^{\text{bond}} = 1.5/Z$ and $p_c^{\text{site}} = 2/Z$ (Sahimi 1994) and $p_c = p_0(Z - 1)^{-a}$. Results on regular lattices (Paterson et al. 2002) showed that these predictions however did not give good correlations for $Z < 6$. As extensive topological analysis of rock core material from a range of geological settings

has shown that the mean coordination number Z is often $Z < 6$, this is of importance in the prediction of residual phase saturations in porous rocks. Moreover, given the broad distributions in Z observed in real rock materials, is the mean coordination number sufficient to predict the trapping threshold on real pore network topologies? These questions have been explored recently by a number of researchers.

Mean Coordination Number Suding and Ziff (1999) first showed the importance of lattice topology other than mean coordination number on percolation thresholds of OP in two dimensions. They considered 11 Archimedian lattices with identical mean coordination numbers. They showed that the mean coordination number alone was not sufficient to predict p_c . Predictions for p_c on these lattices varied from 0.55 to 0.80. Stochastic networks of rock material had previously (Ioannidis et al. 1997) been generated to solely match the coordination number of rocks by diluting sites on a regular cubic lattice until the remaining connected component had the desired mean coordination number. Analysis of the trapping threshold on a diluted cubic network and Fontainebleau sandstone however gave very different thresholds. There was clearly a need to compare networks in 3D with precisely controlled topology. Sheppard developed a 4 part algorithm to generate a network with a specified coordination number distribution (Sok et al. 2002). Use of this algorithm allowed one to generate stochastic networks with matching of mean coordination and the coordination number distribution. Sok et al. (2002) generated an ordered (diamond) network ($Z = 4$) and a range of stochastic networks with an identical mean coordination number $Z = 4$ and different standard deviations in Z ; $\sigma(Z) = 0.0001, 1.0, 2.0$. The trapping threshold for TIP on the lattices differed strongly from the diamond network (see Table 3). The bond TIP threshold for the diamond network and the stochastic network with $\sigma(Z) = 0.001$ varied strongly, while the site TIP threshold varied. Variation of the coordination number distribution led to strong differences in the resultant TIP thresholds. These results showed that thresholds cannot be correlated solely to

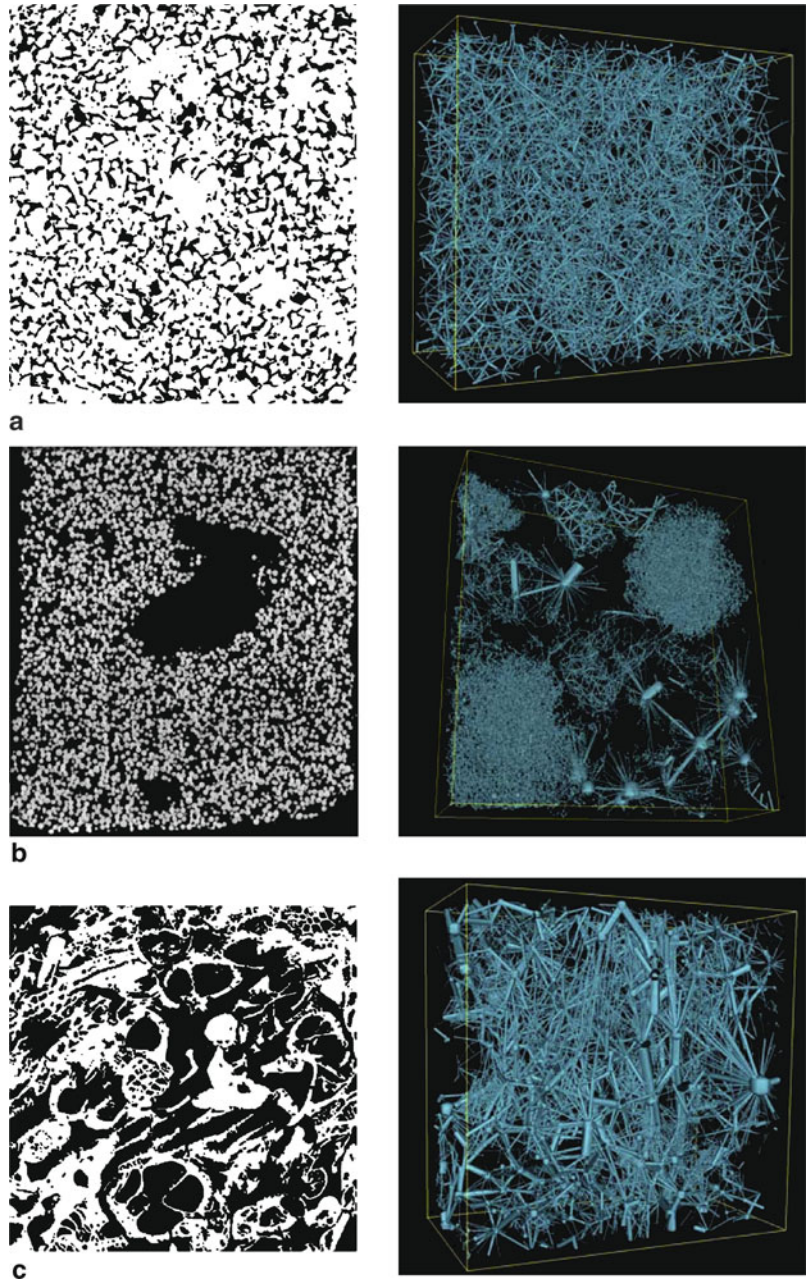


Invasion Percolation, Fig. 2 (a) 2D slice of a 3D image of a sand pack along with the (b) results of a pore partitioning of the sample. (c) shows a small subset of the resultant network of pores and throats in 3D and (d) the

coordination number distribution. (e, f) give geometric information including the pore size distribution and the pore tortuosity

Invasion Percolation,

Fig. 3 Images (*left*) and networks (*right*) of three samples. (a) Castlegate sandstone, (b) bidisperse sample and (c) Mt. Gambier limestone. The size of the pores and throats reflects their actual size in the partitioning of the 3D image. The variation in structure across the three samples is dramatic



dimension and coordination number of the network.

Coordination Number Distribution and Higher Order Measures Rock networks display a broad distribution of coordination number and the presence of long range topological bonds. Recent results have shown (Lee et al. 2004; Sok et al. 2002) that honoring the full coordination

number distribution does lead to better prediction of the trapping IP thresholds than matching the coordination number alone. However differences have still been noted. This result shows that one might require a complete description of the network topology to accurately predict trapping thresholds. One study (Sok et al. 2002) introduced higher order topological quantities; ring size,

Invasion Percolation, Table 2 Details of the network structure for the three samples shown in Fig. 3. Z_m gives the mean coordination number, Z_w the volume weighted mean and $Z_{\max}$ the maximal pore coordination number. The mean $\left(\frac{R_p}{R_t}\right)_m$ and volume weighted $\left(\frac{R_p}{R_t}\right)_w$ pore to throat aspect ratios are also given

Sample	Z_m	Z_w	$Z_{\max}$	$\left(\frac{R_p}{R_t}\right)_m$	$\left(\frac{R_p}{R_t}\right)_w$
Bead Pack	5.1	7.2	19	2.3	3.5
Sandstone	5.4	9.0	49	2.9	4.0
BiDisperse	3.6	31.4	227	3.0	30.3
Limestone	5.6	30.4	372	6.5	20.3

Invasion Percolation, Table 3 Threshold values for the four coordinated lattices

Regular lattice	0.290	0.417
Stochastic: $\sigma = 0.001$	0.298	0.426
Stochastic: $\sigma = 1.0$	0.328	0.429
Stochastic: $\sigma = 2.0$	0.375	0.437

coordination sequence and topological bond length as measures of relevance to the prediction of trapping thresholds. Comparison of these topological properties between rock networks and stochastic networks showed clear differences. A second study (Lee et al. 2004) showed that rock networks exhibited a large proportion of topological long bonds; bonds connecting two pores which are not nearest neighbors. A procedure to add topological long bonds was then developed. The introduction of topological long bonds led to a better match to the higher order measures and a marked effect on the prediction of trapping thresholds. Overall the results illustrate the importance of network topology on the accurate prediction of trapping phase thresholds.

Influence of Pore Geometry on IP Properties The resultant percolation saturations in IP are strongly dependent on the geometric properties of rock, in particular the distributions of sizes and shapes of pores (Larson et al. 1977, 1991; Wilkinson and Willemsen 1983). For an uncorrelated system in which random numbers are assigned to each site/bond, we would expect for IP that most small/large random numbers are accepted as part of the invading cluster, while the

large/small numbers remain part of the defending phase at the final saturation. Unlike OP, where one observes a sharp acceptance profile, in TIP there is a transition region (Wilkinson and Willemsen 1983). From the acceptance profile and the distribution of pore volumes one can estimate the trapped saturation for various pore size distributions.

Influence of Pore Scale Geometric Correlations on IP Properties One can further illustrate the effect of local pore geometry/correlation in real rock structures by randomly rearranging pore volumes on the rock network structure. By doing this one is preserving the topology of the network; only considering the effect of randomizing the pore bodies. The effect of this rearrangement was illustrated for a set of Fontainebleau sandstone samples in Sok et al. (2002). The site-based trapping thresholds were $STIP < 0.25$ for the actual rock samples, while the rearranged sample exhibited trapping thresholds $STIP > 0.45$. These differences are consistent with the presence of local correlated heterogeneity in the pore network at the smallest scales. A method to measure and introduce the spatial heterogeneity observed in the rock structure at a pore scale is lacking; at present the best representations of rock microstructure would be based on true 3D realizations; either from reconstruction method (Bakke and Øren 1997) or from direct measurement of 3D structure via X-ray computed tomography (Dunsmuir et al. 1991; Flannery et al. 1987; Spanne et al. 1994).

Effect of Correlated Heterogeneity on IP

In this section we consider the application of IP to the description of multiphase fluid flow in porous media at scales larger than individual pores. Early work with network models and invasion percolation concentrated on macroscopically homogeneous porous media built using independently generated random numbers to assign pore and throat sizes. Correspondingly most of the testing of the models was conducted on laboratory porous media made from relatively uniform glass spheres

or from uniformly etched glass plates. However it became apparent when strategies for improved oil recovery were attempted in the field that recoveries did not match expectations, largely because of heterogeneity at all scales. This led to studies of heterogeneity and evidence that long-range correlations in properties down to the centimeter (Painter 2001) and the pore scale (Knackstedt et al. 1998; Yuan 1991) exist in many, if not most, porous sedimentary rocks.

Measurement of Heterogeneity

The earliest work that considered correlated substrates used two-dimensional multifractal lattices as a means of incorporating heterogeneity (Meakin 1988, 1991).

Subsequently there have been many studies that have improved understanding of the long-range correlations in rock properties that exist from the pore scale to the kilometer scale. To describe these correlations, fractional Brownian motion (fBm) is one of the models that has been used as a model for the underlying reservoir heterogeneity (Molz et al. 1997). Fractional Brownian motion is straightforward to generate, hence it has been an obvious candidate for studies of percolation in correlated property maps (Babadagli 2000; Du et al. 1995, 1996; Paterson et al. 1996).

Invasion percolation with trapping on substrates with a spatially correlated threshold distribution resulting from the mapping of a self-affine surface has also been studied by Wagner et al. (1997b).

Analysis of sandstones (Knackstedt et al. 1998) on rock samples of a few centimeters in extent suggests that correlated heterogeneity exists down to the pore scale and that at this scale correlations persist at scales up to several pore lengths. For rock samples at these scales a more appropriate model of correlated heterogeneity is one which introduces a cutoff length scale below which correlations persist and above which the system behaves like a random material.

Effect of Heterogeneity on IP

Fractal Dimension The effect of the correlated heterogeneity measured in naturally occurring

sedimentary rocks on IP was first studied in 2D (Meakin 1991; Paterson et al. 1996; Wagner et al. 1997b); the fluid displacement patterns for lattices with long range correlations based on multifractal, fBm and fLm models were compared to uncorrelated networks. The cluster fractal dimension for NTIP was found to be compact for almost all systems exhibiting correlated heterogeneity while TIP exhibited fractal saturation patterns for multifractal systems and fBm models with a Hurst exponent $H < 0.5$. In all studies with fBm model correlations the cluster fractal dimension was observed to increase with $H < 0.5$; for $H > 0.5$ all clusters were compact. This result was verified later (Knackstedt et al. 2000) on large lattices for fBm correlated lattices. Similar results were obtained on 3D lattices (Knackstedt et al. 2000). Other fractal dimensions were also studied; for $H < 0.5$ the fractal dimensions of the hull, minimal path, backbone and invasion front are all fractal with dimensions that depend on H (Babadagli 2000; Knackstedt et al. 2000; Meakin 1991).

The effect of correlated heterogeneity with a finite cutoff length scale for the extent of correlations (correlated heterogeneity at a smaller scale and uncorrelated above some cutoff length scale) has also been considered (Knackstedt et al. 2000). In these cases clusters were fractal at length scale above the cutoff length with fractal dimensions that are the same as those in normal IP models. For smaller length scales the clusters' structures are similar to those observed for fully correlated lattices.

Thresholds Studies in two dimensions have considered the effect of correlated heterogeneity on breakthrough saturations (Babadagli 2000; Du et al. 1996; Meakin 1991) – results on finite lattices showed that correlation has a significant effect on the percolation threshold and that the threshold is no longer unique but depends on the spanning rule employed (Marrink et al. 2000). Residual saturations S_r in 3D systems found that the introduction of correlation leads to a large reduction in residual saturation with increasing H (Knackstedt et al. 2001). For uncorrelated

cubic lattices $S_r = 0.34$, while $S_r = 0.25, 0.22$ and 0.18 for fBm correlated lattices with $H = 0.2, 0.5$ and 0.8 respectively. Correlations with a finite cutoff also led to changes in S_r ; in particular the residual saturation was found to exhibit a minimal value for finite cutoff lengths; the increase in saturations at large cutoff length scales was due to the possibility of trapping very large regions of the defending fluid at larger cutoffs. Small scale correlations therefore have a profound effect on resultant residuals, even at large scales. Analysis of the scaling behavior of the variance of residual saturations shows that the measurements of S_r must be made on samples that are at least ten times larger than the extent of correlated heterogeneity. Measurements on porous rock samples with extensive correlations would lead to a wide variety of S_r being measured. This has been observed experimentally (Paterson et al. 1998).

Trapped Cluster Distribution Introduction of correlated heterogeneity has a strong effect on the resultant distribution of clusters of the trapped defending fluid (Knackstedt et al. 2001). For small-scale correlations one observes the presence of larger clusters of trapped phase. For large scale correlations one or two trapped clusters can account for much of the trapped defending phase saturation. This has important implications to recovery of fluids from rocks under tertiary displacements where a third phase is injected to further reduce the saturation of the defending fluid. The presence of larger residual clusters may make it easier to reconnect and recover the trapped phase.

Stratification and Relative Permeability Extending the work on substrates generated from fractional Brownian motion, Paterson et al. (1998) simulated invasion percolation with anisotropic correlations that were introduced to simulate the stratification often apparent in sedimentary rocks. The anisotropy was created by compressing the property maps in one direction and then deleting layers so the the grid spacing in each direction is equal. In their study invasion percolation was being used as a step to calculate relative permeability in porous media.

The anisotropic heterogeneity led to different sets of relative permeability curves parallel and perpendicular to the bedding direction. This was consistent with experimental observations that relative permeability at a given saturation is greater for flow parallel to the bedding when compared with flow perpendicular to the bedding.

IP in Fractured Systems

Fractured systems differ from granular porous media in that representation by a network of pores (sites) connected via throats (bonds) disappears. Instead a fracture can be represented by a single aperture of varying thickness. Nevertheless, surface roughness within the fracture creates variable capillary pressure in two-phase flow, so it is still possible to apply the invasion percolation concept.

To model flow in fractal fractures, Wagner et al. (2000, 1999) used invasion percolation with trapping on two-dimensional substrates with a correlated distribution of invasion thresholds. Hence their simulations are essentially two-dimensional porous-media flow with heterogeneity. They simulated displacement in the void space between one fBm surface and one plane surface, and studied how fractal scaling behavior depends on the surface roughness. Simulations on fractures consisting of a fBm surface and its displaced replica displayed a cross-over phenomenon. For displacements longer than the correlation length the flow patterns were found to have the properties of ordinary IP clusters grown on uncorrelated substrates.

In a separate line of investigation, Glass et al. (1998) used invasion percolation to model experiments in a synthetic horizontal fracture made from two plates of roughened glass in contact. The aperture field for this fracture was measured using a light absorption technique. To apply invasion percolation they analyzed the correct curvature to use for the fluid invasion steps. A subsequent study by Glass et al. (2004) developed simulations for a fracture patterned on measured data from a block of welded tuff.

Invasion percolation simulations were also matched to experiments by Amundsen et al. (1999). Their experiments involved two different

rough bottom plates with a smooth planar top plate. One of the bottom plates was plastic milled to a self-affine surface with a Hurst exponent of 0.8. The other bottom plate was textured glass measured using a light absorption technique like Glass et al. (1998).

Future Directions

The simple invasion percolation model provides a very realistic simulation of the slow fluid-fluid displacement processes within porous materials. The utility of the model and its variants to important applications are numerous. They include the understanding of contaminant migration in soils crucial to the successful implementation of groundwater remediation strategies. The ability to predict the transport of contaminants in soils will impact on the understanding of water quality issues. After primary oil recovery, more than 50% of the original oil in place remains unrecovered; a significant volume fraction of the pore space occupied by oil and gas is unrecovered because it is bypassed in the rock by the combined effects of the natural water drive mechanism, capillary forces and rock heterogeneity. Realistic estimation of recoveries is a central problem in the development of new fields and in the development of improved oil recovery methods in existing fields. The further development of the invasion percolation model and its variants coupled with a more realistic structural characterization of the pore structure of porous materials will play a crucial role in the development of an understanding of these important problems.

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Conduction and Diffusion in Percolating Systems

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Article Outline

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Glossary

Backbone In a lattice percolation problem above the percolation threshold, that fraction of the infinite cluster with two disjoint connections to infinity.

Correlation length (ξ) Length scale in a randomly structured system over which the system cannot be regarded as homogeneous.

Critical exponent Exponent characterizing the dominant behavior of an observable quantity near a percolation threshold; e.g., $\xi \sim \text{constant} \times (p_c - p)^{-\nu}$ as $p \uparrow p_c$.

Effective medium approximation Approximate description of an inhomogeneous system obtained by matching averaged local fluctuations in properties in a self-consistent manner.

Flux Vector-valued function (in a continuum) or signed scalar (in a discrete system) quantifying transport or conduction rates.

Lattice Discrete structure (network/graph) of sites (nodes/vertices) connected by bonds (links/edges), including periodic lattices, random lattices, and tree-like or self-similar pseudolattices.

Percolation theory Idealized model of a random medium. In the classical discrete case, the bonds of a lattice are independently open with probability p (Bernoulli bond percolation) or the sites of a lattice are independently occupied with probability p (Bernoulli site percolation). There are various continuum analogues.

Percolation threshold (p_c) Dividing point in parameter space separating cases where long-range connectivity is precluded (infinite connected sets exist with probability 0) from those where long-range connectivity occurs (infinite connected sets exist with positive probability).

Percolative system Random two-phase continuous or discrete system in which one phase is deemed void or nonconducting; usually a percolation threshold exists in such systems.

Potential (V) Function distributed over space or over the sites of a network from which steady-state transport or conduction may be determined.

Pseudolattice A nonperiodic discrete structure of sites (nodes/vertices) and bonds (links/edges), most commonly either topologically tree-like or geometrically self-similar.

Random walk Model of random motion, especially on lattices, consisting of a sequence of steps separated by constant or random time intervals.

Recurrent random walk Random walk process on a lattice for which the walker returns to the starting site with probability 1.

Renormalization Converting a system, either exactly or approximately, to a related system with a different characteristic length scale.

Transient random walk Random walk process on a lattice for which the walker has probability less than 1 of returning to the starting site.

Definition of the Subject and Its Importance

The problem of determining the macroscopic structural and transport properties of microscopically

nonuniform materials has a long history and is of such central importance that it finds applications in an astonishingly wide range of areas of science and technology, from developmental biology to xerography (Milton 2002; Sahimi 2003a, b). Consider systems that consist of two phases, each of which is homogeneous in its properties, mixed in some way to create an inhomogeneous material. Let one phase occupy a fraction ϕ of the volume. If $\phi \ll 1$, so that the inhomogeneous structure is in some sense dilute, the possibility arises of determining the effective properties of the material as an expansion in powers of ϕ . Simple examples of this, when the dilute phase consists of identical spheres distributed in some reasonable manner, are the prediction variously associated with the names of Maxwell, Clausius, Mossotti, Lorenz, Lorentz, and others that spheres of dielectric permittivity ϵ_1 embedded in a matrix of permittivity ϵ_0 produce an effective permittivity ϵ^* given by

$$\frac{\epsilon^* - \epsilon_0}{\epsilon^* + 2\epsilon_0} \approx \frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + 2\epsilon_0} \phi; \quad (1)$$

and the prediction of Einstein (1906, 1911) that the effective viscosity η^* of a random suspension of rigid spheres occupying a volume fraction ϕ in a liquid of viscosity η is given by

$$\eta^* = \eta \left[1 + \frac{5}{2} \phi + o(\phi) \right]$$

as $\phi \rightarrow 0$. Analogous calculations can be performed for many other “dilute” systems, leading to predictions at low volume fraction for effective electrical conductivity and other attributes. Simple examples demonstrate that as the volume fraction ϕ increases, quantitative information on exactly how the phases are distributed becomes essential for accurate prediction of, or even construction of decent bounds for, effective properties – knowing the volume fractions of the phases is not enough.

We address inhomogeneous systems and especially two-phase systems – both continua and lattices – that are randomly structured, with particular emphasis on systems in which only one phase (with relative abundance ϕ) sustains

transport. The simplest such models arise by defining steady-state transport processes or random motions on the occupied phase in the lattice percolation model (chapter ▶ [“Percolation Phase Transition”](#) by M. Sahimi in this handbook) of Broadbent and Hammersley (Broadbent and Hammersley 1957; Hammersley 1957a, b, 1961) or its continuum analogues (chapter ▶ [“Principles of the Theory of Continuum Percolation”](#) by I. Balberg in this Encyclopedia). We call all such models *percolative models*. They exhibit threshold behavior at $\phi = \phi_c$, separating globally nonconducting states when the transport-sustaining phase is sufficiently rare ($0 \leq \phi < \phi_c$) from conducting states when the transport-sustaining phase is sufficiently abundant ($\phi_c < \phi \leq 1$). When the transport-sustaining phase only sparsely spans a large region, that is, just above the percolation threshold ϕ_c , asymptotic power-law dependence of the transport properties on $\phi - \phi_c$ is observed, but many results now deemed well-known still evade rigorous proof.

Introduction

We address problems of transport and conduction, both in continua and on lattices, where there are randomly distributed local transport properties, especially the cases where there are two phases present (for continua) or there are bonds or sites of two types present (for lattices). Although we later pay most attention to the lattice case, for the present and in section [“Continuum Models: Steady-State Phenomena”](#) we discuss primarily continua in which two material phases with different properties are present. Frequently, one of these phases is empty space (void space). Within regions comprising only one phase, all properties of the system are uniform. The properties of regions containing both phases depend not only on the relative proportions of each phase present, but also on the way the phases are distributed. The fundamental question to be answered is this: if we pretend that the system is homogeneous, as it might indeed appear if we viewed a very large piece of it from a distance, what are the effective transport properties of the system?

A complete solution of the problem is not to be expected if the microstructure is elaborate or especially subtle, but sufficient progress has been made since the 1950s that for a number of conceptually simple models, some exact results and many approximate results of decent quality are available. The two cases amenable to treatment are periodic microstructure and random microstructure. The former case, which is not our present concern, presents few conceptual challenges and is increasingly amenable to numerical calculation, since the determination of the global properties of the system can usually be reduced to a study of a single finite region (the fundamental repeat unit) and this is usually computationally tractable.

Interest in modeling systems in which small (usually identical) pieces of one phase are randomly distributed in some way and the remaining phase occupies the rest of space goes back at least to James Clerk Maxwell (1831–1879), Ludvig Valentin Lorenz (1829–1891), and Hendrik Antoon Lorentz (1853–1928). The work of these authors in the latter half of the nineteenth century and some antecedents, culminating in results such as Eq. (1), is reviewed by Landauer (1978), Markov (2000), and Milton (2002). In the first two decades of the twentieth century, the problem was addressed by Einstein (1906, 1911) and others, but four major conceptual developments were needed to bring the subject beyond its infancy.

- (a) Bruggeman (1935), building on ideas of earlier authors but arguing with much greater clarity, developed an *effective medium approximation*, in which an unknown overall property of the composite system, such as its effective conductivity σ_{eff} , is computed in an approximate but self-consistent manner that takes account of fluctuations in the corresponding local property. In the extreme case in which one phase is nonconducting, Bruggeman's approach predicts that for sufficiently small volume fraction ϕ of the conducting phase, there is no conductivity, but there is a critical volume fraction ϕ_c of the conducting phase above which there is conduction, with effective conductivity

$$\sigma_{\text{eff}} \sim \text{constant} \times (\phi - \phi_c) \text{ as } \phi \downarrow \phi_c.$$

Bruggeman's original treatment pays no attention to the manner in which the phases are randomly or periodically distributed.

- (b) Beran (1965, 1968) established the foundations of a statistical study of effective properties of random media, in which the random placement of phases is statistically quantified. In particular, Beran brought out the importance of considering individual realizations of a random system equipped with a proper probability structure and drew attention to the important issue of ergodicity, which in this context concerns the relation between volume averages (averages of properties over large volumes in a single realization) and ensemble averages (averages over many realizations).
- (c) Broadbent and Hammersley (1957) and Hammersley (1957a, b, 1961) considered a lattice model of random media, motivated by a problem of gas mask design for British coal miners. Although quantified transport was not part of their original model – they only addressed connectivity – this work is at the conceptual heart of modern discussions. In their model, now known as *percolation theory*, the lattice is randomly stripped so that either individual bonds remain with probability p (bond percolation) or individual sites remain with probability p (site percolation); the parameter p is the analogue of volume fraction ϕ in a two-phase random continuum, with what remains of the lattice viewed as a conducting phase in the original system. There is a well-defined relative abundance p of the conducting phase, called the *percolation threshold* p_c , above which there is long-distance connectivity and transport is possible. Although the percolation threshold plays for the lattice model a role analogous to the critical volume fraction predicted by Bruggeman's effective medium approximation (and indeed effective medium approximations can be set up for lattice systems), the existence of a precise percolation threshold p_c was rigorously established in 1957, and its value is known exactly for some lattices

and approximately but to very high precision for other lattices. The probability that a given site belongs to an infinite connected cluster of the active phase when that phase has relative abundance p is the percolation probability $P_\infty(p)$, and it is accepted that $P_\infty(p) \sim \text{constant} \times (p - p_c)^\beta$ as $p \downarrow p_c$, with $\beta = 5/36$ in simple two-dimensional lattice systems and $\beta \leq 1$ more generally. A number of the techniques and concepts that have developed over 50 years for lattice-based percolation theory have now found their way into natural continuous-medium analogues (Meester and Roy 1996). Both the lattice and continuum percolation models have many applications (Milton 2002; Sahimi 1994, 2003a; Torquato 2002).

- (d) That percolation ideas would be significant in physics was realized almost immediately (Anderson 1958) following the 1957 paper of Broadbent and Hammersely. The final conceptual step needed was first articulated by Ziman (1968): the stochastic geometry underlying percolation theory, though essential to the description of transport in random media, does not completely characterize the transport properties: there is also the specific contribution of the transport mechanism. The natural attempt to connect a transport coefficient such as effective conductivity $\sigma_{\text{eff}}(p)$ to the percolation probability $P_\infty(p)$ by writing $\sigma_{\text{eff}}(p) \propto P_\infty(p)$ (Eggarter and Cohen 1970) was refuted by experiments of Last and Thouless (1971) on the conductivity of a sheet of colloidal graphite with holes randomly punched in it in a manner appropriate to simulate site percolation on the square lattice. The experiments suggested that

$$\sigma_{\text{eff}}(p) \sim \text{constant} \times (p - p_c)^t \text{ as } p \downarrow p_c,$$

with $t > 1 \gg \beta$. The subtlety of the problem arises from the fact that just above the percolation threshold, the sample-spanning structure is tenuous and tortuous, with significant implications on observable quantities that characterize the transport process.

The developments stemming from the approximate work of Bruggeman and the rigorous work

of Beran [(a) and (b) above] are well covered in the expansive texts of Milton (2002) and Torquato (2002). The bulk of the present chapter is devoted to random medium problems – both continuous and discrete, though favoring the latter – with a percolative aspect [(c) and (d) above]. Steady-state continuum problems are discussed first in section “Continuum Models: Steady-State Phenomena,” with the physical contexts addressed in section “Contexts.” These contexts are also claimed by advocates of the analogous lattice models discussed in section “Lattice Models: Steady-State Phenomena,” to which we pay more attention. The model on which we primarily focus is the *random resistor network* (introduced in section “The Random Resistor Problem”), which reveals most of the key features of random media, especially the existence of percolation thresholds and the subtlety of the active paths in the system close to the percolation threshold. Although many important and elegant results are now available for geometrical and topological aspects of the underlying percolation process, as discussed in the books by Bollobás and Riordan (2006a), Grimmett (1999) and Hughes (1996), and (Sahimi’s chapter ▶ “Percolation Phase Transition” in this Encyclopedia), considerable work is still needed to resolve major questions concerning the random resistor network and related systems.

We do not consider the mechanical properties (such as elastic moduli or fracture resistance) of random media, although many of the ideas and results presented here have been extended to mechanical properties in the literature. Less restricted surveys of the properties of random media can be found in the major texts of Milton (2002), Sahimi (2003a, b), and Torquato (2002). Time-evolving problems in randomly structured media are of great interest, but our discussion in section “Random Motion in a Random Environment” is restricted to a brief discussion of diffusion processes in random continua, followed by a more expansive discussion of discrete-time and continuous-time random walk processes on lattices with some form of random spatial variation in the probability distribution governing steps between nearest-neighbor sites. Particular emphasis is placed on the model of random walk on a

random lattice derived from a percolation process, poetically described as the *ant in the labyrinth* (Brandt 1975; de Gennes 1976a; Hughes 1996).

Continuum Models: Steady-State Phenomena

Despite the enormous efforts expended on discrete inhomogeneous and percolative systems, most scientific applications that motivate these studies arise in materials perhaps most naturally treated as continua. We briefly summarize several contexts in which percolative systems arise and review selected findings for continua that expose major concepts later discussed more extensively for the more tractable discrete analogues. Examples considered

- (i) are scalar, so that we have scalar transport coefficients rather than tensors;
- (ii) involve real potentials, so we consider only steady direct current electrical conduction, rather than frequency-dependent alternating current conduction;
- (iii) have no explicit time dependence;
- (iv) have linear constitutive response.

The reader may refer to the expansive texts of Milton (2002) and Sahimi (2003a, b) for discussions without the restrictions (i)–(iv).

Contexts

Problems Equivalent to Electrical Conduction

In a variety of physical contexts, the following mathematical problem arises. Let Ω be a domain (a connected spatial region), let $\sigma(\mathbf{r})$ (which we shall call a *transport coefficient*) be a prescribed function of position $\mathbf{r}$ in Ω , and let ∇ denote the usual gradient operator. We are to find a *potential* $V(\mathbf{r})$ that satisfies the equation

$$\nabla \cdot (\sigma \nabla V) = 0, \mathbf{r} \in \Omega, \quad (2)$$

subject to prescribed conditions on the boundary $\partial\Omega$ of Ω , usually either the Dirichlet boundary condition [$V(\mathbf{r})$ prescribed], the Neumann

boundary condition [$\mathbf{n} \cdot \nabla V$ prescribed, where $\mathbf{n}$ is a unit vector normal to $\partial\Omega$ and, for consistency, the surface integral of $\mathbf{n} \cdot \nabla V$ over $\partial\Omega$ is zero], or Dirichlet and Neumann conditions applied to disjoint components of $\partial\Omega$. The potential V , which is uniquely defined for the Dirichlet boundary-value problem and is unique (up to an additive constant for the pure Neumann boundary-value problem), is associated with a vector field

$$\mathbf{E} = -\nabla V, \quad (3)$$

and the field $\mathbf{E}$ and the transport coefficient σ determine a flux vector

$$\mathbf{J} = \sigma \mathbf{E}. \quad (4)$$

Equation (2) can be interpreted as a statement of a conservation law under steady-state conditions for a substance carried by the flux vector $\mathbf{J}$. Where the transport coefficient has surfaces of discontinuity (as is the case in two-phase media), one interprets the partial differential equations as holding in the distributional sense and the boundary conditions of continuity of V and of $\mathbf{n} \cdot \sigma \nabla V$ (where $\mathbf{n}$ is normal to the phase interface) follow.

The canonical example of the problem embodied in Eqs. (2), (3), and (4) is steady state (direct current) electrical conduction, with V the electrostatic potential, $\mathbf{E}$ the electric field, $\mathbf{J}$ the electric current, and σ the electrical conductivity. Six different interpretations of the same mathematical problem are given in Table 1. For the first three interpretations, the potential V is the consequence of a fundamental physical equation of the form $\nabla \times \mathbf{E} = 0$. In the remaining examples in Table 1, the flux law $\mathbf{J} = \sigma \mathbf{E}$ and the potential–field relation $\mathbf{E} = -\nabla V$ do not have individual fundamental physical interpretations.

Caveats to the Electrical Interpretation

In our discussion we shall use the terminology appropriate to electrical conductivity, however in interpreting the results in other contexts several caveats are needed. For time-dependent diffusive processes, we really wish to solve the *diffusion equation*

Conduction and Diffusion in Percolating Systems, Table 1 Mathematically equivalent potential theory problems

Transport coefficient	Flux law	Potential–field relation
Electrical conductivity σ	$\mathbf{J} = \sigma \mathbf{E}$	$\mathbf{E} = -\nabla V$ from Maxwell's $\nabla \times \mathbf{E} = 0$
Dielectric permittivity ϵ	$\mathbf{D} = \epsilon \mathbf{E}$	$\mathbf{E} = -\nabla V$ from Maxwell's $\nabla \times \mathbf{E} = 0$
Magnetic permeability μ	$\mathbf{B} = \mu \mathbf{H}$	$\mathbf{H} = -\nabla V$ from Maxwell's $\nabla \times \mathbf{H} = 0$
Transport coefficient	Flux–potential relation	
Thermal conductivity κ	Fourier's Law (temperature T)	$\mathbf{Q} = -\kappa \nabla T$
Diffusivity D	Fick's Law (concentration c)	$\mathbf{j} = -D \nabla c$
Permeability k	Darcy's Law (pressure P , viscosity η)	$\mathbf{q} = -(k/\eta) \nabla P$

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c). \quad (5)$$

The electrical conduction analogue applies only to the steady state. Similar issues arise for heat conduction. For diffusion, problems in which the tracer is injected at an isolated point (a point source) are of great interest. In the extreme case in which one phase sustains diffusion and the other does not, the effect of placing the source at an arbitrary point in the phase that sustains diffusion depends critically on whether the source falls in a conducting region of finite extent or of infinite extent and these issues are not covered by a discussion confined to the electrical conduction analogue.

Although we have included porous medium permeability in Table 1, this exact equivalence to the electrical conduction problem only applies when we work at length scales large compared to pore sizes, so that the notion of permeability – whether constant or variable – is meaningful. A problem of great interest arises when one considers fluid flow through the void space of a medium consisting of an impermeable solid phase and a void phase (Sahimi 1995). In this case, there is no local partial differential equation at all for the solid phase, while in the void space the fluid is subject to the low Reynolds number limit of the Navier-Stokes equations.

The Idea of Homogenization

If the local conductivity σ is bounded, but fluctuates in some manner, one may seek a “homogenized” description of the medium, replacing the variable conductivity problem $\nabla \cdot (\sigma \nabla V) = 0$ by a uniform conductivity problem $\nabla \cdot (\sigma_{\text{eff}} \nabla V) = 0$ that matches it in some sense that needs to be made

precise, with the constant *effective conductivity* σ_{eff} to be determined. A porous medium, viewed as a two-phase void/solid system as mentioned above, homogenizes in a different manner, since the equations for the desired uniform system, embodying Darcy's Law, are structurally different from the equations that govern the flow in the pore space (Sahimi 1995). We do not discuss this case here.

There are two basic rigorous approaches. One, on which we focus in the present chapter, is introduced in section “Effective Conductivities.” The other, which is generally described as *homogenization theory*, may be briefly summarized as follows. There are three length scales in the problem: a microscale, on which the structure fluctuates (perhaps strongly), a mesoscale over which unstructured continuum behavior emerges, and a macroscale over which parameters defined at the mesoscale may vary slowly. One may define volume averages $\langle \mathbf{E} \rangle$ and $\langle \mathbf{J} \rangle$ of the electric field over some representative domain large compared to the length scale on which microstructure fluctuates (i.e., a mesoscale domain) and introduce a homogenized conductivity $\hat{\sigma}$ defined by

$$\langle \mathbf{J} \rangle = \hat{\sigma} \langle \mathbf{E} \rangle. \quad (6)$$

Homogenization is successful if, in an appropriate limit as the microscale dimension is sent to zero, a well-defined $\hat{\sigma}$ emerges. The theory of homogenization has been well worked out for periodic microstructures (Allaire 1992; Bensoussan et al. 1978), which are not our concern here, but is more challenging for the random microstructure case, although considerable progress has also been made there (Golden and Papanicolaou 1983; Jikov et al. 1994); surveys of recent work will be

found in the texts of Milton (2002) and Torquato (2002). The first strong results were derived for uniformly elliptic partial differential operators, which in the present context means that for some constants α and β we have $0 < \alpha \leq \sigma \leq \beta < \infty$, precluding the analysis of percolative systems, but extensions to percolative systems are discussed in the book of Jikov, Kozlov, and Oleinik (1994). Percolative systems are subtle because the length scale on which the inhomogeneity is important – the correlation length – diverges at the percolation threshold; and the detailed geometrical arrangement of the conducting and nonconducting phases is very important except perhaps for very low or very high volume fractions of the conducting phase. It should be emphasized that in homogenizing random media, the determination of exact values of $\hat{\sigma}$, either by formula or in terms of an algorithm for easy, highly precise computation, largely remains a distant goal. Establishing the existence of a well-defined $\hat{\sigma}$ and determining any of its nontrivial qualitative properties is already a major achievement.

Effective Conductivities

As an alternative to the homogenization approach outlined above, one may simply define effective properties of an inhomogeneous system by a black box approach. In the electrical analogy, and considering three dimensions for definiteness, take a finite rectangular prism $-M < x < M$, $-M < y < M$, $0 \leq z \leq L$, occupied by the inhomogeneous conductor, with all boundaries save for $z = 0$ and $z = L$ being insulated ($\mathbf{n} \cdot \sigma \nabla V = 0$). If one specifies the potential to be $V = V_0$ at $z = 0$ and $V = 0$ at $z = L$, and the z -component of the current through the surface $x = 0$ is $J(x, y)$ per unit area, then a reasonable definition of the effective conductivity σ_{eff} is

$$\sigma_{\text{eff}} = \lim_{L \rightarrow \infty} \lim_{M \rightarrow \infty} \frac{1}{V_0/L} \int_{-M}^M \int_{-M}^M \frac{J(x, y) dx dy}{(2M)^2}, \quad (7)$$

where L/M is held constant as $L, M \rightarrow \infty$. This is the most natural definition for physical experiments or computer simulation and the one we adopt below in our more detailed discussion of discrete models. Actually, for a randomly

structured two-phase system, unless one establishes that for the particular statistical model of the microstructure, the limit is well-defined and takes the same value for almost all realizations of the microstructure (i.e., the limit exists and takes a unique value with probability 1), the integral has to be averaged over all realizations of the microstructure before the limit $L, M \rightarrow \infty$ is taken.

An alternative definition replaces the insulated boundary conditions on all faces other than $z = 0$ or $z = L$ by $V = V_0(L - z)/L$. One could alternatively set up a definition of effective conductivity by prescribing a uniform injection of current per unit area across the face $z = 0$ and studying the induced potential difference.

Golden and Papanicolaou (1983) have examined the relation between the black box definition of effective conductivity for a finite region and the definition from homogenization and shown their equivalence under the conditions of uniform ellipticity. Stronger results applicable to percolative systems will be found in Jikov et al. (1994).

While results on the existence of a well-defined effective conductivity σ_{eff} are of course of significant interest, one really wants to determine its value.

Exact Results

Few nontrivial exact results on the effective conductivity are available. Consider a one-dimensional conductor of length L , comprising N independent random conducting elements of length Δ , with the k th element having conductivity σ_k and sustaining a potential drop V_k . Then the current flowing is $J = \sigma_k V_k / \Delta$, the same in each element, and the field is

$$\frac{1}{L} \sum_{k=1}^N V_k = \frac{1}{N\Delta} \sum_{k=1}^N \frac{J\Delta}{\sigma_k} \rightarrow J \langle \sigma^{-1} \rangle, \quad (8)$$

where we have taken the limit $N \rightarrow \infty$ and used the Strong Law of Large Numbers (Feller 1971). Hence we have the exact result that

$$\sigma_{\text{eff}} = \frac{1}{\langle \sigma^{-1} \rangle}. \quad (9)$$

For two-dimensional systems, there are a number of “phase interchange” or “duality” results, due

to Keller (1964) and others, discussed carefully by Milton (2002). In particular, an infinite chessboard, with the white squares having conductivity σ_w and the black squares having conductivity σ_b , produces an exact effective conductivity

$$\sigma_{\text{eff}} = \sqrt{\sigma_w \sigma_b}. \quad (10)$$

Bounds

The electrical energy dissipation rate associated with a potential distribution V and corresponding electric field $\mathbf{E}$ and current $\mathbf{J}$ in the finite $2M \times 2M \times L$ rectangular prism of section “Effective Conductivities” is

$$\begin{aligned} \varepsilon\{V\} &= \int_{-M}^M \int_{-M}^M \int_0^L \mathbf{J} \cdot \mathbf{E} \, dx dy dz \\ &= \int_{-M}^M \int_{-M}^M \int_0^L \sigma |\nabla V|^2 \, dx dy dz. \end{aligned} \quad (11)$$

Consider a potential V that satisfies the partial differential equation $\nabla \cdot (\sigma \nabla V) = 0$ in the interior and the boundary conditions $V = V_0$ on $z = 0$, $V = 0$ on $z = L$ and $\mathbf{n} \cdot \sigma \nabla V = 0$ on other surfaces: we call this an *admissible potential*. Let W , a *trial potential*, be any other function that satisfies the same boundary conditions but may not satisfy the partial differential equation. If we write $\eta = W - V$, expand $\varepsilon\{W\} = \varepsilon\{V + \eta\}$ and use the Divergence Theorem and the boundary conditions, we easily show that $\varepsilon\{W\} \geq \varepsilon\{V\}$, so that admissible potentials minimize energy dissipation. That is, we have a variational principle. It can be shown under reasonable conditions that

$$\sigma_{\text{eff}} \leq \frac{1}{(V_0/L)^2 (2M)^2 L} \int_{-M}^M \int_{-M}^M \int_0^L \sigma |\nabla W|^2 \, dx dy dz, \quad (12)$$

so that trial potentials can be used to construct rigorous upper bounds on the effective conductivity. A complementary variational principle that leads to lower bounds on the effective conductivity can be derived by analyzing trial current distributions. The variational approach has its origin in work of Brown (1955) and has been developed in diverse contexts by many authors (Brown, Beran, Prager, Hashin and

Shtrikman, Davies, ...) with varying degrees of rigor (Milton 2002; Torquato 2002). Bergman (1978) introduced an alternative approach to variational methods for deriving bounds on effective conductivities, based on complex variable techniques. Bergman’s work and many important consequences are reviewed by Milton (2002).

The most easily derived bounds hold without restriction on the distribution of phases in a multi-phase system and also apply for continuously varying local conductivities:

$$\frac{1}{\langle \sigma \rangle} \leq \sigma_{\text{eff}} \leq \langle \sigma \rangle, \quad (13)$$

where angle brackets denote the volume average. These bounds, first identified in 1912 by Wiener (1912), are the best possible general bounds, since they become equalities in the case of slabs of homogeneous material parallel to the face $z = 0$ (conductors in series – $\sigma_{\text{eff}} = 1/\langle \sigma^{-1} \rangle$) or no variation in conductivity with z (conductors in parallel – $\sigma_{\text{eff}} = \langle \sigma \rangle$). If no additional assumptions are made except for statistical isotropy, the 1962 bounds of Hashin and Shtrikman (1962) become the best possible. For high and low conductivity phases with volume fractions ϕ_{high} and ϕ_{low} and conductivities $\sigma_{\text{high}} \geq \sigma_{\text{low}}$, the Hashin–Shtrikman bounds in d dimensions ($d = 2$ or 3) are

$$\begin{aligned} \sigma_{\text{low}} + \frac{d\phi_{\text{high}}\sigma_{\text{low}}(\sigma_{\text{high}} - \sigma_{\text{low}})}{d\sigma_{\text{low}} + \phi_{\text{low}}(\sigma_{\text{high}} - \sigma_{\text{low}})} &\leq \sigma_{\text{eff}} \\ &\leq \sigma_{\text{high}} - \frac{d\phi_{\text{low}}\sigma_{\text{high}}(\sigma_{\text{high}} - \sigma_{\text{low}})}{d\sigma_{\text{high}} - \phi_{\text{high}}(\sigma_{\text{high}} - \sigma_{\text{low}})}. \end{aligned} \quad (14)$$

If we consider the case of a percolative system, where we have $\sigma_{\text{low}} = 0$, $\sigma_{\text{high}} = \sigma_1$ and for brevity we write $\phi_{\text{high}} = \phi$ (i.e., ϕ is the volume fraction for the conducting phase) the lower bounds in (13) and (14) become trivial ($\sigma_{\text{eff}} \geq 0$) and neither upper bound is very strong, as shown by Fig. 1. For the case of spheres with independently located centers (technically, Poisson points) and either constant radii, or random radii with a reasonable distribution, it can be rigorously established (Meester and Roy 1996) that for sufficiently small ϕ , the probability that there is an infinite connected region of

the conducting phase is zero and consequently the effective conductivity will be zero below a percolation threshold ϕ_c . Numerical simulations with Poisson-centered conducting spheres of constant radius show that $\phi_c \approx 0.2895 \pm 0.0005$ (Rintoul and Torquato 1997): the grey rectangle in Fig. 1 spans the interval $0 \leq \phi \leq \phi_c$ for this system, and parts of the upper bound curves (13) and (14) that intersect the grey rectangle miss the threshold behavior entirely and are misleadingly uninformative for this specific system.

In Fig. 1, we also show as discs numerical estimates (Kim and Torquato 1992) of the conductivity in the case where the randomly placed spheres are nonconducting, the rest of space is conducting and the percolation threshold is much smaller ($\phi_c \approx 0.03$ (Kim and Torquato 1992)); physicists call this the *Swiss cheese model*. The Hashin–Shtrikman upper bound (14) works better because the percolation threshold is so low, but the Hashin–Shtrikman lower bound remains useless. Much better bounds than those shown are available for nonpercolative

problems, especially if additional information about correlations between phase locations is available (Milton 2002; Torquato 2002).

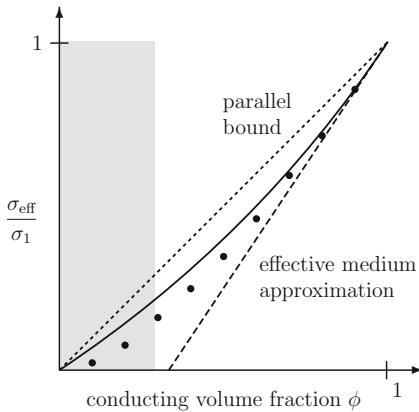
Approximations

Clarifying work of earlier authors, Bruggeman (1935) derived an *effective medium approximation* for the effective conductivity. This approach represents an uncontrolled approximation – it does not give rigorous bounds and a priori estimation of its accuracy is not possible. One considers a spherical inclusion of unspecified constant conductivity within a uniform medium whose conductivity is taken to be the unknown effective conductivity σ_{eff} , which will be estimated “self-consistently.” For a prescribed constant field $\mathbf{E}$ at infinity, the field within the inclusion is calculated. The requirement that, when averaging over material properties within the inclusion, the average field in the inclusion does not differ from the field at infinity yields an approximate equation for σ_{eff} ,

$$\left\langle \frac{3\sigma_{\text{eff}}}{\sigma + 2\sigma_{\text{eff}}} \right\rangle = 1. \quad (15)$$

In the case in which $\sigma = \sigma_1$ with probability ϕ , corresponding to a volume fraction ϕ of the conducting phase, this approximation predicts that for a percolative system

$$\phi_{\text{eff}} = \frac{3}{2} \left(\phi - \frac{1}{3} \right) \sigma_1. \quad (16)$$



Conduction and Diffusion in Percolating Systems,

Fig. 1 Bounds on the effective conductivity σ_{eff} for a conducting phase of conductivity σ_1 randomly and homogeneously distributed at volume fraction ϕ , with remaining space occupied by a nonconducting phase. The grey area lies below the percolation threshold estimate $\phi_c \approx 0.2895 \pm 0.0005$ of Rintoul and Torquato (1997) for overlapping conducting spheres in a nonconducting matrix. The solid discs are numerical estimates of Kim and Torquato (1992) for overlapping nonconducting spheres in a conducting matrix, where $\phi_c \approx 0.03$. Upper broken line: elementary (“parallel”) bound $\sigma_{\text{eff}}/\sigma_1 \leq \phi$. Solid curve: Hashin–Shtrikman bound $\sigma_{\text{eff}}/\sigma_1 \leq 2\phi/(3 - \phi)$ (Hashin and Shtrikman 1962). Lower broken line: effective medium approximation $\sigma_{\text{eff}}/\sigma_1 \approx (3/2)(\phi - 1/3)$ for $\phi \geq 1/3$ from work of Bruggeman (1935)

The physical requirement that $\sigma_{\text{eff}} \geq 0$ leads one to interpret this as predicting that $\sigma_{\text{eff}} = 0$ for $0 \leq \phi \leq 1/3$, so that there is a threshold for the conductivity at $\phi = 1/3$.

As shown in Fig. 1, this approximation closely conforms to the Hashin–Shtrikman upper bound near $\phi = 1$. Although it has the desirable feature of predicting a conductivity threshold, the actual predicted threshold (1/3) is not particularly close to numerical estimate for randomly placed spheres with independent centers (0.2895) and is very far from the estimated threshold for the Swiss cheese model (0.03).

Differences Between Continuum and Discrete Models

The considerable emphasis in the literature on discrete (lattice) models is partly motivated by the folklore of *universality*, under which, apart from some reasonable conditions that exclude direct, long-range connections and other oddities, qualitative features, and associated critical exponents of analogous problems depend only on dimensionality. While this appears to be broadly true, there are some significant exceptions, two of which we mention here.

- (a) A parameter value where properties of the infinite system which are elsewhere analytic lose analyticity is called a *critical point*. In the percolation model (Broadbent and Hammersley 1957; Hammersley 1957a, b, 1961) on periodic lattices, there is only one critical point associated with global connectedness (Men'shikov 1986), namely, the percolation threshold, and this coincides with the only critical point for the effective conductivity. Following on work of Kozlov (1989), Jikov et al. (1994) have discussed carefully a random chessboard, where the plane is divided into equal squares, colored independently. Squares are black (conductivity σ_b) with probability ϕ and white (conductivity σ_w) with probability $1 - \phi$. For $\phi = 1/2$, Eq. (10) holds, but more importantly, in the random chessboard model there are effectively two thresholds for a given color, one for long-distance connectivity using corner connections and one for long-distance connectivity through adjoining edges of the squares. If we let $p_c \approx 0.59$ denote the site percolation threshold of the square lattice (chapter ► “Exact Percolation Thresholds” by J.C. Wierman in this Encyclopedia), then the following results hold as $\sigma_b \rightarrow 0$ with σ_w held fixed. For $0 \leq \phi \leq 1 - p_c$, the white phase has large components connected via edges of squares and

$$\lim_{\sigma_b \rightarrow 0} \sigma_{\text{eff}} = \sigma_w f(\phi) > 0.$$

For $1 - p_c < \phi < p_c$ neither color has large components connected via edges of squares,

but both colors have large components connected via corners, and

$$c_1(\phi)\sqrt{\sigma_w\sigma_b} \leq \sigma_{\text{eff}} \leq c_2(\phi)\sqrt{\sigma_w\sigma_b}.$$

For $p_c < \phi < 1$, we have $\sigma_b \leq \sigma_{\text{eff}} \leq c_3(\phi)\sigma_b$. Berlyand and Golden (1994) have established the stronger result that for $1 - p_c < \phi < p_c$, $\sigma_{\text{eff}} = \sqrt{\sigma_w\sigma_b} + O(\sigma_b)$ as $\sigma_b \rightarrow 0$ with σ_w held fixed. Torquato et al. (1999) have reported numerical studies.

- (b) The universality concept presupposes that all analogous systems in the same dimension have the same critical exponents for a given system property. Thus, for example, in a percolative continuous system where ϕ is the volume fraction of the conducting phase, we expect to see

$$\sigma_{\text{eff}} \sim \text{constant} \times (\phi - \phi_c)^t \text{ as } \phi \downarrow \phi_c. \quad (17)$$

where the conductivity exponent t (the general existence of which remains to be established, even for specific two and three dimensional systems) is independent of microstructure, and the same for lattices and continua in a given dimension. This expectation turns out to be wrong, with hopes being dashed by computational studies of Feng et al. (1987) on the Swiss cheese model introduced in section “Bounds”: in two dimensions the lattice and Swiss cheese continuum model exponents are close together and possibly coincident; in three dimensions the exponent t for the Swiss cheese continuum is about 0.5 larger than the exponent t for the simple cubic lattice.

Lattice Models: Steady-State Phenomena

Notwithstanding the caveats exposed in section “Differences Between Continuum and Discrete Models,” we turn to a detailed discussion of discrete systems. We consider *lattices* (also known as networks or graphs) of *sites* (also known as nodes or vertices) connected by *bonds* (also called links or edges). The number of bonds attached to a site is its *coordination number* (also called degree or

valence), and two sites that are attached to the same bond are called *nearest-neighbor sites*. The most commonly studied lattices are periodic in structure, the simplest example being the *hyper-cubic lattice* $\mathbb{Z}^d$ of sites with integer coordinates, connected by bonds of unit length, so that each site has coordination number $2d$. Other important infinite networks are sometimes called *pseudolattices* to distinguish them from periodic structures. The most important examples of pseudolattices are self-similar or fractal structures (Mandelbrot 1982) (chapter ► “Scaling Theory of Percolation Clusters” by D. Stauffer in this Encyclopedia) and tree-like structures, especially the *Cayley tree* or *Bethe lattice* (Thorpe 1982) of coordination number z , in which there are no closed loops.

The graphical distance between two sites is defined to be number of bonds in the shortest path that links the sites. It is customary to define a ball of radius $\rho \in \mathbb{N}$ centered on site $\mathbf{s}$ to consist of all sites at graphical distance ρ or less from $\mathbf{s}$ and the surface sites of the ball to be those sites of the ball that have at least one nearest-neighbor site outside the ball. If the number of boundary sites of the ball is asymptotically negligible compared to the total number of sites in the ball as $\rho \rightarrow \infty$, then the lattice or pseudolattice is said to be an amenable graph. Tree-like pseudolattices provide examples of nonamenable graphs and exact results for random environment problems on them are not necessarily qualitatively representative of the corresponding attributes of periodic lattices.

Key Results from Percolation Theory

In percolation theory for lattices, sites are declared *occupied* or *vacant* in some random way and bonds are declared *open* or *closed* in some random way. A site is deemed to belong to a cluster of size $n \geq 1$ (where n may be finite or infinite) if it is present and connected via open bonds to $n - 1$ other sites; a vacant site is a cluster of size 0. In the (Bernoulli) *bond problem*, all sites are occupied, and bonds are independently declared open with probability p and closed with probability $1 - p$. In the (Bernoulli) *site problem*, sites are occupied with probability p and vacant with probability

$1 - p$, and a bond is declared open if and only if the two sites it joins are both occupied. Every bond percolation problem is equivalent to a site percolation problem on a related lattice, so that it suffices to state general results for site percolation, although in many examples modeling transport and conduction, the language of bond percolation is more appropriate.

Viewed at sufficiently low resolution, a realization of bond or site percolation other than at the percolation threshold appears homogeneous. A measure of the length scale over which inhomogeneous structure is important is furnished by the *correlation length* $\xi(p)$. A way to define $\xi(p)$ precisely on $\mathbb{Z}^d$ is to let τ_m denote the probability that the sites at $\mathbf{0}$ and $(m, 0, 0, \dots, 0)$ belong to a common finite cluster. Then

$$\xi(p) = -\lim_{m \rightarrow \infty} m^{-1} \ln \tau_m.$$

Rigorous General Results

The following results are rigorously proven (Bollobás and Riordan 2006a; Grimmett 1999; Hughes 1996) for Bernoulli site percolation, provided that the lattice or pseudolattice is homogeneous in the sense that all sites are equivalent (as is the case for $\mathbb{Z}^d$ and the Bethe lattice), and the number of sites at most n bonds distant from a given site grows no faster than $c \exp(an^\kappa)$, where $a > 0$, $c > 0$ and $\kappa < 1$.

- (i) There exists a percolation threshold $p_c > 0$ such that the probability $P_\infty(p)$ of a chosen site belonging to an infinite cluster is zero for $p < p_c$ and strictly greater than zero for $p > p_c$.
- (ii) The probability $P_n(p)$ that a chosen site belongs to a cluster of size n decays exponentially rapidly with increasing n when $p < p_c$.

The exponential decay of $P_n(p)$ ensures the finiteness of the *mean cluster size*

$$\chi(p) = \sum_{n=0}^{\infty} n P_n(p)$$

for $p < p_c$. The sum remains meaningful for $p > p_c$ if we exclude the infinite cluster $n = \infty$ and

$$\chi(p)/(1 - P_\infty(p))$$

becomes the mean cluster size, conditioned on the cluster being finite. A result related to (ii) establishes that on $\mathbb{Z}^d$, the correlation length is well-defined and finite for $p < p_c$.

- (iii) The mean cluster size $\chi(p)$ is finite for $p < p_c$ but $\chi(p) \geq pp_c(p_c - p)^{-1}$ when $p < p_c$, so that $\chi(p) \rightarrow \infty$ as $p \uparrow p_c$.
- (iv) For a given value of p , there is a number k_0 (which may take no values other than 0, 1 or ∞) such that the number of distinct infinite clusters of occupied sites on the lattice takes the value k_0 with probability 1. When $P_\infty(p) = 0$, $k_0 = 0$.

For some pseudolattices, such as the Bethe lattice, if $0 < P_\infty(p) < 1$ then $k_0 = \infty$. However, for a class of lattices which includes normal periodic lattices, if $P_\infty(p) > 0$ then $k_0 = 1$, that is, when an infinite cluster exists it is unique.

- (v) For $p > p_c$ a site is part of the *backbone* if it lies on the infinite cluster, and within that cluster there are two independent paths to infinity. If $B(p)$ is the probability that a given site belongs to the backbone then $B(p) \leq p^{-1}P_\infty(p)^2$.

For a discussion of the determination of and actual values of site and percolation thresholds for particular lattices, see chapter ► “[Exact Percolation Thresholds](#)” by J.C. Wierman in this Encyclopedia.

Heuristics

A heuristic scaling theory for percolation theory (chapter ► “[Scaling Theory of Percolation Clusters](#)” by D. Stauffer in this Encyclopedia) introduced in 1979 by Stauffer (1979) and analogies between percolation and statistical mechanics first exhibited in 1972 by Fortuin and Kasteleyn (Fortuin 1972; Fortuin and Kasteleyn 1972) lead to the following folklore (Hughes 1996). There are *critical exponents* that describe the non-analytic behavior of important attributes of the percolation model at the percolation threshold. If

we use the proportionality symbol $\propto$ as a short notation, so that $f(p) \propto g(p)$ as $p \rightarrow p_c$ means that $f(p)/g(p) \rightarrow$ nonzero constant, then the critical exponents are defined as follows:

cluster size distribution at p_c

$$P_n(p_c) \propto n^{-1-1/\delta} \quad \text{as } n \rightarrow \infty; \quad (18)$$

mean cluster size below p_c

$$\chi(p) \propto (p_c - p)^{-\gamma} \quad \text{as } p \uparrow p_c; \quad (19)$$

mean size of finite clusters above p_c

$$\chi(p) \propto (p_c - p)^{-\gamma'} \quad \text{as } p \downarrow p_c; \quad (20)$$

correlation length below p_c

$$\xi(p) \propto (p_c - p)^{-\nu} \quad \text{as } p \uparrow p_c; \quad (21)$$

correlation length above p_c

$$\xi(p) \propto (p_c - p)^{-\nu'} \quad \text{as } p \downarrow p_c; \quad (22)$$

percolation probability p_c

$$P_\infty(p) \propto (p - p_c)^\beta \quad \text{as } p \downarrow p_c; \quad (23)$$

backbone probability

$$B(p) \propto (p - p_c)^{\beta_{bb}} \quad \text{as } p \downarrow p_c. \quad (24)$$

For the Bethe lattice, it is established that $\delta = 2$, $\gamma = 1$, $\beta = 1$ and $\beta_{bb} = 2$ (Hughes 1996), but for standard lattices even the existence of critical exponents in the sense explained above is not rigorously established, although as noted below, a few weaker results consistent with this picture, such as $\lim_{p \downarrow p_c} \ln [P_\infty(p)] / \ln (p - p_c) = \frac{2}{36}$ for site percolation on the triangular lattice, are now proven. Many of the proofs of such rigorous results as we have are both long and difficult, but Duminil-Copin and Tassion (2016a, b) have shown how some known but previously hard-to-obtain results can be proven in a few pages, including the inequality

$$P_\infty(p) \geq p^{-1}(p - p_c)/(1 - p_c) \text{ for } p > p_c$$

and the exponential decay of the cluster size distribution for $p < p_c$ in bond percolation on $\mathbb{Z}^d$.

Folklore asserts that exponents are the same for the all site and bond problems in a given dimension (universality), vary significantly with the dimension d in low dimensions, and are independent of dimension for $d \geq 6$, where they take the so-called *mean-field values* $\beta = \gamma = 1$ and $\nu = \frac{1}{2}$. These values were rigorously established by work of Hara and Slade (1994) for standard percolation for $d \geq 19$, and for a spread-out model of percolation for $d \geq 6$, and have been subsequently shown to hold for standard percolation for $d > 10$ (Fitzner and van der Hofstad 2017). At $d = 6$, the prefactors in the dominant asymptotic forms that define the critical exponents may be modified by the inclusion of a power of $\ln |p - p_c|$. It is generally believed that $\gamma = \gamma'$ and $\nu = \nu'$. On modest hypotheses on lattice structure, it is rigorously established (Hughes 1996) from work of various authors that, provided the exponents exist, $\beta \leq 1$, $\gamma \geq 1$, $\gamma/d \leq \nu \leq \gamma$, and $\nu \geq 2/d$, but two much more informative scaling relations are accepted:

$$\gamma + 2\beta = \beta(\delta + 1) \quad (25)$$

in all cases, and for $d \leq 6$,

$$d\nu = 2\beta + \gamma. \quad (26)$$

All credible numerical evidence supports the existence of critical exponents consistent with these scaling laws, they are rigorously established for site percolation on the triangular lattice (Smirnov and Werner 2001), and natural probabilistic conditions equivalent to (26) for bond percolation on $\mathbb{Z}^d$ are known (Borgs et al. 1999).

In most theoretical and numerical studies of percolation, the lattice or pseudolattice on which site or bond percolation is realized is highly regular (a periodic lattice, or a self-similar or tree-like structure). However, a number of results are available for percolation on lattices created by applying the Voronoi tessellation algorithm to a set of points randomly generated by a spatial Poisson process, and no significant differences to the

accepted view of percolation on periodic lattices have yet been encountered in Voronoi percolation (Ahlberg et al. 2016; Bollobás and Riordan 2006b; Duminil-Copin et al. 2017; Tassion 2016; Vanneuville 2019).

Rigorous Results for Two Dimensions

For several two-dimensional lattices, a number of exact results are known: in particular $p_c = 1/2$ for site percolation on the triangular lattice (coordination number 6) and bond percolation on the square lattice (coordination number 4). In these particular problems, it has also been rigorously established that the percolation probability $P_\infty(p)$ is continuous for $0 \leq p \leq 1$, so that there is no infinite cluster present right at the percolation threshold. This result is believed to be true, but remains unproven, in three dimensions.

Major innovations in probability since 2000, primarily associated with the work of Lawler, Schramm, Smirnov, and Werner, have led to the following results being rigorously established for the case of site percolation on the two-dimensional triangular lattice (Smirnov and Werner 2001; Werner 2009):

$$P_\infty(p) = \left(p - \frac{1}{2}\right)^{5/36+o(1)} \text{ as } p \downarrow \frac{1}{2}; \quad (27)$$

$$\chi(p) = \left|p - \frac{1}{2}\right|^{-43/18+o(1)} \text{ as } p \rightarrow \frac{1}{2}; \quad (28)$$

$$\xi(p) = \left|p - \frac{1}{2}\right|^{-4/3+o(1)} \text{ as } p \rightarrow \frac{1}{2}. \quad (29)$$

This is almost (but not quite) a proof of existence of critical exponents in the sense of physicists, and moreover shows that the scaling relations (25) and (26) hold in this one particular case and the accepted folklore for two dimensions that

$$\beta = \frac{5}{36}, \gamma = \gamma' = \frac{43}{18}, \nu = \nu' = \frac{4}{3}, \quad (30)$$

arrived at from scaling arguments, statistical mechanical arguments, heuristic arguments and numerical evidence, is indeed correct in this one

particular case. The exact backbone exponent β_{bb} remains unknown, but it has been shown to be determined by the leading eigenvalue of a differential operator (Lawler et al. 2002). It has been established rigorously that if certain critical exponents defined at the percolation threshold exist, then the values of each of these exponents are the same for bond percolation on the square, triangular, and hexagonal lattices (Grimmett and Manolescu 2013), adding further support for belief in universality of critical exponents for reasonable lattices in a given dimension.

The Random Resistor Problem

The canonical discrete model of transport and conduction is the *random resistor network*, in which the bonds of a lattice or some less regular network are resistors of random resistance. A more extended discussion of this model, including proofs of many results stated here, will be found in Hughes (1996); for the Dirichlet, Thomson and Rayleigh Principles discussed below see also Doyle and Snell (1984). The first study of random resistor networks may fairly be ascribed to Kirkpatrick (1971, 1973), although an equivalent system had already been studied as early as 1956 by Fatt (1956) as a model for porous media, with hydraulic conductivities of bonds playing the role of resistance and pressure playing the role of voltage.

Problem Definition

If we use Greek subscripts to index bonds of the lattice (each bond being assigned a nominal direction of orientation), then the (direct) current I and the potential difference V across a particular bond α are related by Ohm's Law $I = G_\alpha V$, where G_α is the conductance of bond α (the reciprocal of the resistance). Current is a signed quantity. If the potential at site $\mathbf{s}'$ is less than that at site $\mathbf{s}$ then the current flowing from $\mathbf{s}$ to $\mathbf{s}'$ is positive.

It is customary to assume that the conductances of different bonds are independent, identically distributed random variables. Note that one might consider more generally the case in which $I = G_\alpha(V)$ where G_α is a nonlinear function with several random parameters, but this problem is both subtle (Calvert and Keady 1993) and difficult

(Blumenfeld et al. 1986, 1987; Gu and Yu 1992; Kenkel and Straley 1982; Meir et al. 1986; Straley and Kenkel 1984) and will not be discussed here; see Sahimi (2003b).

If the bonds of a random resistor network have independent, identically distributed conductances governed by the probability density function

$$f(g) = (1-p)\delta_+(g) + ph(g), 0 < p < 1, \quad (31)$$

where $h(g)$ is the conditional probability of the conductance, given that the conductance is non-zero, we call the network the *general percolation conduction problem*. We use the notation $\delta_+(g)$ to distinguish a delta function that acts on the right from the usual symmetric delta function $\delta(x)$. The specific case in which $h(g) = \delta(g - g_0)$, that is,

$$f(g) = (1-p)\delta_+(g) + p\delta(g - g_0), 0 < p < 1, \quad (32)$$

will be called the *standard percolation conduction problem*. The definitions (31) and (32) are directly associated with bond percolation. A standard percolation problem for site percolation arises on assigning each bond that links two occupied sites the conductance g_0 , and making all other bonds nonconducting.

In general, we have a lattice with a potential (voltage) V_s at each site $\mathbf{s}$ and a current i_{rs} flowing from site $\mathbf{r}$ to site $\mathbf{s}$ along a bond of conductance $G_{rs} = G_{sr}$ (equivalently, resistance $R_{rs} = 1/G_{rs}$). From Ohm's Law

$$i_{rs} = G_{rs}(V_r - V_s) \quad (33)$$

and Kirchhoff's Law of conservation of current $\sum_s i_{rs} = I_r$, we have

$$\sum_s G_{rs}(V_r - V_s) = I_r, \quad (34)$$

where I_r is the current supply into site $\mathbf{r}$, positive if current is injected and negative if it is withdrawn. At most sites $\mathbf{r}$, we have $I_r = 0$, but we impose the additional physical requirement that $\sum_r I_r = 0$, the sum being taken over all sites where current is injected or withdrawn. When appropriate boundary conditions are imposed on finite pieces of periodic lattice, or on finite networks more

generally, the problem is completely specified and numerical determination of the potential distribution over the sites and the associated currents is possible; from this estimates of an effective conductivity σ_{eff} that we define in section “[Lattices of Dimension \$d \geq 2\$](#) ” below emerge.

Bounds for General Resistor Networks

Before addressing the specific case of periodic lattices, we consider arbitrary finite networks. The *effective conductance* $C_{\text{ab}}^{\text{eff}}$ between two sites **a** and **b** and its reciprocal, the *effective resistance* $R_{\text{ab}}^{\text{eff}}$ between the sites, are defined by

$$C_{\text{ab}}^{\text{eff}} = \frac{1}{R_{\text{ab}}^{\text{eff}}} = \frac{I}{V_{\text{a}} - V_{\text{b}}}, \quad (35)$$

if a current I injected at site **a** and withdrawn at site **b** is associated with a potential difference $V_{\text{a}} - V_{\text{b}}$ between the sites. (Effective conductivities arise by scaling effective conductances with appropriate measures of network size.) Variational principles enable bounds on the effective conductance to be deduced.

Dirichlet's Principle. Consider a finite resistor network with bond conductances

$$G_{\text{rs}} \text{ (where } 0 \leq G_{\text{rs}} \leq \infty \text{)}$$

and with a specified potential difference V between sites **a** and **b**. Let $\{W_{\text{s}}\}$ be a *trial potential distribution*, that is, any set of real numbers subject to the requirement that $W_{\text{a}} - W_{\text{b}} = V$. Let $\{V_{\text{s}}\}$ be an *admissible potential distribution*, that is, a set of real numbers satisfying the Kirchhoff–Ohm Law (34) for $\text{s} \neq \text{a}$ or **b**, as well as the constraint $V_{\text{a}} - V_{\text{b}} = V$. Then the effective conductance between sites **a** and **b** is given by

$$\begin{aligned} C_{\text{ab}}^{\text{eff}} &= \frac{1}{2V^2} \sum_{\text{r}, \text{s}} G_{\text{rs}} (V_{\text{r}} - V_{\text{s}})^2 \\ &\leq \frac{1}{2V^2} \sum_{\text{r}, \text{s}} G_{\text{rs}} (W_{\text{r}} - W_{\text{s}})^2. \end{aligned} \quad (36)$$

Thomson's Principle. Consider a finite resistor network with bond resistances

$$R_{\text{rs}} \text{ (where } 0 \leq R_{\text{rs}} \leq \infty \text{)}$$

and a specified current I_{a} injected at site **a** and withdrawn at site **b**. Let $\{j_{\text{sr}}\}$ be a *trial current distribution*, that is: $j_{\text{rs}} = -j_{\text{sr}}$; $\sum_{\text{s}} j_{\text{rs}} = 0$ if $\text{r} \neq \text{a}$ and $\text{r} \neq \text{b}$; and $\sum_{\text{s}} j_{\text{as}} = I_{\text{a}} = -\sum_{\text{s}} j_{\text{bs}}$. Let $\{i_{\text{sr}}\}$ be an *admissible current distribution*, that is, a trial current distribution for which Ohm's Law

$$V_{\text{r}} - V_{\text{s}} = i_{\text{rs}} R_{\text{rs}}$$

holds. Then the effective resistance between sites **a** and **b** is given by

$$R_{\text{ab}}^{\text{eff}} = \frac{1}{2I_{\text{a}}^2} \sum_{\text{r}, \text{s}} i_{\text{rs}}^2 R_{\text{rs}} \leq \frac{1}{2I_{\text{a}}^2} \sum_{\text{r}, \text{s}} j_{\text{rs}}^2 R_{\text{rs}}. \quad (37)$$

The sums in the inequalities in Dirichlet's and Thomson's Principles may be interpreted as the rate of energy dissipation corresponding to the potential distribution or the current distribution respectively. These two principles assert that admissible potential and current distributions minimize the rate of energy dissipation. From these two principles, a number of important results follow, including the following.

Rayleigh's Monotonicity Principle. For finite resistor networks, the resistance between two sites does not decrease if the resistances of some or all of the bonds are increased.

Exactly Solvable Models

In one dimension, N random resistors in series yield an effective conductivity (here the overall conductance per unit length) $\sigma_{\text{eff}} = \langle G^{-1} \rangle^{-1}$; the argument is the same as that used above for a random one-dimensional continuum. A slightly less trivial problem for which exact results are available is the standard percolation conduction problem on a Bethe lattice or Cayley tree of coordination number z (Heinrichs and Kumar 1975; Hughes 1996; Stinchcombe 1973, 1974). Pick an arbitrary site s_0 of the lattice, set that site to have potential V_0 , and prescribe that the potential is zero at the periphery of the tree (i.e., the potential decays asymptotically to zero as we move outwards from s_0 along any infinite path of open

bonds that may be present). If a current I_0 flows from site $\mathbf{s}_0$ into the tree, then the tree conductance may be defined as $T = I_0/V_0$. Where the average is taken over all realizations of the system, it can be proved that $\langle T \rangle$ is zero for $p < p_c = (z - 1)^{-1}$ and

$$\langle T \rangle \sim \frac{2zg_0c}{z-2} [p(z-1) - 1]^2 \text{ as } p \downarrow p_c, \quad (38)$$

where $c \approx 0.761$ is a constant. Since $p_c = 1/(z - 1)$ for the Bethe lattice, this result is consistent with the hypothesis that long-distance conduction is possible in the standard percolation conduction problem (32) if and only if $p > p_c$. It is sometimes argued that the Bethe lattice correctly represents the critical behavior of periodic lattices of sufficiently high dimensionality and that would imply that effective conductivity σ_{eff} defined in section “[Lattices of Dimension \$d \geq 2\$](#) ” satisfies $\sigma_{\text{eff}} \propto (p - p_c)^2$ as $p \downarrow p_c$. Straley (1977a) has identified the flaw in this argument – in a Bethe lattice of finite size, a significant fraction of all sites are at the boundary – and has given a definition of the effective conductivity σ_{eff} of a Bethe lattice that gives bonds in all regions of the lattice comparable significance and leads to $\sigma_{\text{eff}} \propto (p - p_c)^3$ as $p \downarrow p_c$.

For some remarks concerning self-similar pseudolattices for which exact results are available, see section “[Conduction on Fractals](#).”

Lattices of Dimension $d \geq 2$

For random resistor problems more appropriately related to transport and conduction problems in d -dimensional space, we consider periodic lattices. There have been numerical investigations of the standard percolation conduction on topologically random lattices created by the Voronoi algorithm (Jerauld et al. 1984a, b), but we shall not pursue these extensions of the theory.

Defining the Conductivity

Consider the specific case of a finite hypercube Λ_L cut from the simple hypercubic lattice $\mathbb{Z}^d$, with $(L + 1)^d$ sites at locations $\mathbf{s} = (s_1, s_2, \dots, s_d)$ with integer coordinates subject to the inequalities $0 \leq s_j \leq L$. The faces $s_1 = 0$ and $s_1 = L$ are

subjected to a potential difference V , so that there is a potential gradient V/L . In three dimensions, this corresponds to a cubic array of conducting elements sandwiched between two perfectly conducting plates. Boundary conditions on the other faces should be unimportant when L is large, but in numerical work periodic boundary conditions are often used (the faces $s_j = 0$ and $s_j = L$ are joined for $j = 2, \dots, d$). If a total current I flows in response to the imposed potential difference, then the current per unit area (i.e., per site) of the face $s_1 = 0$ is $I/(L + 1)^{d-1}$. We therefore define the (specific) conductivity of the lattice as

$$\lim_{L \rightarrow \infty} \frac{I/(L + 1)^{d-1}}{V/L} = \lim_{L \rightarrow \infty} \frac{L^{2-d}I}{V}. \quad (39)$$

For the random resistor network, one needs to discuss the existence of this limit for each realization ω of the lattice and one is especially interested in the mean value of the limit, which we take as defining the *effective conductivity* of the system:

$$\sigma_{\text{eff}} = \lim_{L \rightarrow \infty} \langle L^{2-d}I/V \rangle = \lim_{L \rightarrow \infty} \langle L^{2-d}C_L \rangle, \quad (40)$$

where $C_L = I/CV$ is the conductance between the faces of the hypercube Λ_L .

For a considerable period, the existence of a well-defined effective conductivity remained unproven, with the case of percolative problems providing an especially severe challenge, but this hurdle was eventually overcome (Jikov et al. 1994). In particular, for percolative problems, it is now established that there is a well-defined $\sigma_{\text{eff}}(p)$. The averages over realizations in Eq. (40) can be dropped, with the limit existing with probability 1, and being 0 for $p < p_c$ and strictly positive for $p > p_c$.

The existence of a well-defined effective conductivity in the infinite lattice size limit essentially guarantees that large differences between the value of the conductivity estimate inferred from a particular realization of a large random resistor network and σ_{eff} are unlikely to be encountered, but making this more precise is a challenging problem on which little progress has yet been

made. The best results to date appear to be those of Biskup et al. (2014), who establish that for a sufficiently narrow distribution of bond conductances (with the minimum conductance strictly positive, so that percolation phenomena are excluded), suitably scaled deviations from σ_{eff} converge in law to a zero-mean Gaussian distribution, but the variance of this distribution is not determined in a manner conducive to ready estimation for a given bond conductance distribution.

Bounding the Conductivity

The Dirichlet and Thompson Principles and Rayleigh's Monotonicity Law are stated for the case in which current is injected at one site and withdrawn at another, but by introducing appropriate links of zero resistance, the laws apply equally well to the case in which a potential difference V is maintained across two parallel faces of the hypercube Λ_L used in the definition of the effective conductivity, and a current I flows between the parallel faces.

The Series and Parallel Bounds. For a random resistor network on the simple hypercubic lattice $\mathbb{Z}^d$ with independent, identically distributed bond conductances, the conductance C_L between two parallel faces of the hypercube Λ_L satisfies the inequalities

$$L^{-1}(L+1)^{d-1}\langle G^{-1} \rangle^{-1} \leq \langle C_L \rangle \leq L^{-1}(L+1)^{d-1}\langle G \rangle, \quad (41)$$

where the random variable G corresponds to the conductance of any one bond of the lattice.

Hence, $\langle L^{2-d}C_L \rangle$ is bounded above as $L \rightarrow \infty$ if the individual bond conductances G have finite mean and is also bounded away from zero if the individual bond resistances $(1/G)$ have finite mean. Under these conditions, if σ_{eff} exists, then from Eq. (40), we have

$$\langle G^{-1} \rangle^{-1} \leq \sigma_{\text{eff}} \leq \langle G \rangle. \quad (42)$$

Hammersley (1988) has used Dirichlet's Principle to derive some stronger results than the series and parallel bounds (42) for independent conductances. Chayes and Chayes (1986) used

variational principles to derive a not directly useful lower bound on the conductivity for the standard percolation conduction problem, and the following more encouraging upper bound.

Upper Bound of Chayes and Chayes. For the standard bond percolation conduction problem on the d -dimensional hypercubic lattice, with open bonds having conductance g_0 , the effective conductivity $\sigma_{\text{eff}}(p)$ satisfies the inequality

$$\sigma_{\text{eff}}(p) \leq g_0 \Pr\{\text{a given bond is part of the backbone}\}. \quad (43)$$

The *conductivity exponent* for the percolation conduction problem is defined by writing

$$\sigma_{\text{eff}}(p) \propto (p - p_c)^t \text{ as } p \downarrow p_c. \quad (44)$$

There is no rigorous proof, even in two dimensions, of the existence of the critical exponent, even in the weak sense that

$$t = \lim_{p \downarrow p_c} \ln [\sigma_{\text{eff}}(p)] / \ln (p - p_c).$$

However, from the result (v) in section “[Rigorous General Results](#)” and the upper bound of Chayes and Chayes, we know that the conductivity is identically zero below the percolation threshold, as one's intuition demands, and if the accepted critical exponents do exist, then we have the inequality

$$t \geq \beta_{\text{bb}} \geq 2\beta, \quad (45)$$

where β_{bb} is the *backbone exponent* and β is the exponent for the percolation probability $P_\infty(p)$. From numerical estimates $\beta_{\text{bb}} \approx 0.52$ in two dimensions, and we know that $2\beta = \frac{5}{18} \approx 0.28$, while $t > 1$ (see section “[Numerical Estimates of the Conductivity Exponent \$t\$](#) ”), so neither inequality is very sharp.

If, instead of a network of resistors and insulators, we consider a network of zero resistance elements (superconductors) with probability p and finite resistance elements (finite conductance g_0) with probability $(1 - p)$, then the *superconductivity exponent* can be introduced by writing

$$\sigma_{\text{eff}}(p) \propto (p_c - p)^{-s} \text{ as } p \uparrow p_c. \quad (46)$$

Scaling Theory for the Conductivity

Straley (1976) developed a heuristic scaling argument to describe the conductivity of a random resistor network for which the probability density function for the individual bond conductances is

$$f(g) = (1 - p)\delta(g - a) + p\delta(g - b), \quad (47)$$

where $a \ll b$. The effective conductivity σ_{eff} changes in the obvious manner when the units of conductivity or length change. A prefactor μ in the conductivity can be regarded as accounting for this. Straley proposed that σ_{eff} is a homogeneous function near the percolation threshold:

$$\sigma_{\text{eff}}(p) \approx \mu S([p - p_c]\lambda^{-1}, a\mu^{-1}\lambda^{-A}, \mu b^{-1}\lambda^{-B}), \quad (48)$$

with the approximation assumed valid when each argument of S is less than unity. The function S is singular when any of its arguments vanishes. The parameter λ embodies the interrelations via scaling of the parameters a , b , and $p - p_c$. Setting $a = 0$, $\lambda = |p - p_c|$ and $\mu = \lambda^B b$ gives

$$\sigma_{\text{eff}}(p) \approx |p - p_c|^B b S(\text{sgn}[p - p_c], 0, 1). \quad (49)$$

This case describes the conductivity of the classical percolation conduction problem, so we are led to the conclusion that $S(-1, 0, 1) = 0$ and $S(1, 0, 1) > 0$, and we identify B with the conductivity exponent t . If instead we set $1/b = 0$, $\lambda = |p - p_c|$ and $\mu = \lambda^{-A} a$, we obtain

$$\sigma_{\text{eff}}(p) \approx |p - p_c|^{-A} a S(\text{sgn}[p - p_c], 1, 0). \quad (50)$$

This case describes the superconductivity problem in which a fraction $1 - p$ of the bonds are normal conductors, while the remaining bonds have infinite conductance, so we conclude that $S(-1, 1, 0) < \infty$ and $S(1, 1, 0) = \infty$ and we identify A with the superconductivity exponent s . Thus,

$$\sigma_{\text{eff}}(p) \approx \mu S([p - p_c]\lambda^{-1}, a\mu^{-1}\lambda^{-s}, \mu b^{-1}\lambda^{-t}). \quad (51)$$

If we now take $p = p_c$ and $0 < a < b < \infty$, then setting $\lambda^{t+s} = a/b$ and $\mu = b\lambda^t$, we obtain

$$\sigma_{\text{eff}}(p_c) \approx a^u b^{1-u} S(0, 1, 1), \quad (52)$$

where the exponent u is given by

$$u = t/(s + t). \quad (53)$$

Special Results for Two Dimensions

Each two-dimensional lattice L with well-defined faces (polygons with the bonds as sides, not crossed by any bonds) is associated with a dual lattice L^D , obtained by placing a site of L^D in every face of L and joining sites of L^D by bonds if the original faces of L share a common bond in L . The square lattice is its own dual lattice; the triangular lattice and the hexagonal lattice form a dual pair. Duality is central to the exact determination of percolation thresholds in two dimensions (chapter ► “Exact Percolation Thresholds” by J.C. Wierman in this Encyclopedia), but also has useful implications for the random resistor problem (Bernasconi et al. 1977; Marchant and Gabillard 1975; Straley 1977b), which parallel the phase interchange relations for two-dimensional continua (section “Effective Conductivities”). For the square lattice, if the probability density function for bond conductances is

$$f(g) = (1 - p)\delta(g - a) + p\delta(g - b), \quad (54)$$

then the effective conductivity $\sigma_{\text{eff}}(p)$ satisfies the equation

$$\sigma_{\text{eff}}(p)\sigma_{\text{eff}}(1 - p) = ab, \quad (55)$$

and in particular $\sigma_{\text{eff}}(\frac{1}{2}) = \sqrt{ab}$. In the notation of Straley’s scaling theory (section “Scaling Theory for the Conductivity”), this implies that $u = \frac{1}{2}$ for the square lattice, and so $s = t$ for the square lattice. Although this does not prove rigorously that the conductivity exponent t and superconductivity exponent s coincide for the square lattice, it

is taken as evidence for the claim that $s = t$ for all reasonable two-dimensional lattices. Numerical evidence is strongly against this result remaining true in higher dimensions.

It can also be shown from duality that for the square lattice, if

$$f(g) = \frac{1}{gD\sqrt{2\pi}} \exp \left[-\frac{(\log g - \log g_0)^2}{2D^2} \right], \quad (56)$$

then $\sigma_{\text{eff}} = g_0$.

Effective Medium Approximations

The effective medium ideas of section “[Approximations](#)” were adapted to the estimation of the conductivity of random resistor networks on periodic lattices by Kirkpatrick (1971, 1973). A much fuller modern account than given here of the implementation of effective medium ideas for lattice systems and the application of the ideas to more subtle problems and in different contexts will be found in Sahimi (2003a).

The random network is replaced by a network that is uniform with unknown bond conductance g_* , except for one special bond, which has conductance G . Let the lattice have coordination number z . It can be shown that the average fluctuation in current or potential difference across the special bond due to its differing in conductance from g_* vanishes provided that

$$\left\langle \frac{G - g_*}{g_* + (2/z)(G - g_*)} \right\rangle = 0, \quad (57)$$

and this gives a self-consistent approximate determination of g_* . For the square and simple cubic lattices, g_* is an approximation for σ_{eff} . For other lattices, σ_{eff} is a constant multiple of g_* . In the case of a percolative conductance distribution, the approximation produces an estimate of the percolation threshold.

For the standard percolation conduction problem (32), where a fraction p of the bonds has nonzero conductance g_0 , the effective medium approximation produces

$$g_*/g_0 \approx (p - 2/z)/(1 - 2/z)$$

and as bond conductances must be nonnegative this prediction is interpreted as meaning that

$$\frac{g_*}{g_0} \approx \begin{cases} 0, & p \leq 2/z, \\ \frac{p - 2/z}{1 - 2/z}, & p > 2/z. \end{cases} \quad (58)$$

That is, the effective medium approximation predicts that the percolation threshold is $2/z$. This is fortuitously exact for the square lattice bond problem and reasonable for the triangular bond and honeycomb bond problems (chapter ▶ “[Exact Percolation Thresholds](#)” by J.C. Wierman in this Encyclopedia), but works less well in three dimensions. The construction of effective medium approximations for site percolation problems is more delicate (Hughes 1996).

The major qualitative deficiency of the effective medium approximation is the conductivity exponent prediction: it asserts that $t = 1$ for all dimensions. This is already a poor approximation in two dimensions ($t \approx 1.3$ – see Table 2) and is grossly misleading in three dimensions ($t \approx 2$ – see Table 3). The effective medium approximation also predicts that the critical exponent is unchanged if the standard percolation conduction problem is replaced by the more general model (31), provided that the mean resistance of conducting bonds is finite, that is,

$$\int_0^\infty g^{-1} h(g) dg < \infty. \quad (59)$$

When the conditional probability density function for the conductance of bonds of nonzero conductance has the asymptotic form $h(g) \propto g^{-\alpha}$ as $g \downarrow 0$ with $0 < \alpha < 1$, so that the condition (59) is violated, the effective medium approximation predicts that $t = 1/(1 - \alpha)$ (Hughes 1996; Kogut and Straley 1979).

The effective medium approximation works well in nonpercolative systems and in percolative systems has some use when p is close to 1.

Conduction and Diffusion in Percolating Systems, Table 2 Estimates of the conductivity (t) and superconductivity (s) exponents in two dimensions. Estimates from physical experiments and from numerical simulations are displayed separately. Where values of both t/v and t , or both s/v and s are given, these values of t/v or s/v were obtained first by finite-size scaling or related ideas, and the values of t or s were subsequently deduced. In two dimensions, it

is known that $v = \frac{4}{3}$ exactly (asterisked entries use this value to compute t or s from t/v or s/v), and also that $s = t$ exactly, but no such results are available for $d = 3$. For the molecular trajectory algorithm (Cen et al. 2012a), the first way analyses motion on all clusters at $p = p_c$, while the second analyses motion on the incipient infinite cluster at $p = p_c$.

t/v	t	Experiment type and source
0.95 ± 0.05	$\approx 1.26^*$	Photolithography on metal films (Palevski and Deutscher 1984)
	1.32 ± 0.25	Nanoscale bismuth clusters (Dunbar et al. 2003)
t/v	t	Numerical technique and source
0.95 ± 0.01	1.28 ± 0.03	Transfer matrix (Derrida and Vannimenus 1982)
0.968 ± 0.005	$\approx 1.291^*$	Transfer matrix (bond) (Zabolitzky 1984)
	1.291 ± 0.024	Random walk simulation ($p > p_c$) (Poole and Salt 1996)
0.970 ± 0.009	$\approx 1.293^*$	Enumerate random walks on backbone (Hong et al. 1984)
0.971 ± 0.005		Molecular trajectory first way (Cen et al. 2012a)
≈ 0.972	$\approx 1.296^*$	Random walk simulation (Rammal et al. 1984)
$0.973^{+0.005}_{-0.003}$	$1.297^{+0.007}_{-0.004}$	Finite-size scaling (Lobb and Frank 1984)
0.975 ± 0.005	$\approx 1.300^*$	Transfer matrix (site) (Zabolitzky 1984)
0.977 ± 0.008		Molecular trajectory second way (Cen et al. 2012a)
0.979 ± 0.006	$\approx 1.305^*$	Finite-size scaling (Rammal et al. 1985)
	1.31 ± 0.04	Monte Carlo (Fogelholm 1980)
0.9826 ± 0.0008	$1.3100 \pm 0.0011^*$	Finite-size scaling (bond and site) (Grassberger 1999)
s/v	s	Numerical technique and source
0.9745 ± 0.0015	1.299 ± 0.002	Special purpose computer (Normand et al. 1988)
0.977 ± 0.010	$\approx 1.303^*$	Transfer matrix (Herrmann et al. 1984)

Renormalization

By analogy with statistical mechanics applications, any process by which a lattice system is replaced by a similar lattice with bonds of different lengths is called (*real-space* or *position-space*) *renormalization*. Such a process can be performed exactly on some self-similar pseudolattices, but not on standard periodic lattices.

Numerical estimates of the effective conductivity based on simulation of finite lattice fragments often use an algorithm in which a finite subnetwork is replaced by a single effective bond for which the conductance may be calculated exactly (Clerc et al. 2000; Grassberger 1999; Lobb and Frank 1979). This is especially effective near the percolation threshold and is sometimes loosely described as an exact renormalization procedure (Clerc et al. 2000). The name is a little misleading, since the new random resistor network cannot generally be embedded in a natural way within the original underlying lattice structure.

There was considerable interest in real-space renormalization in the 1970s and 1980s, as it gave approximate predictions for critical exponents that differ from the so-called mean-field (high dimension) values of the geometrical exponents of percolation theory and from the effective medium predictions of the conductivity exponent. Like the effective medium approximation, real-space renormalization is an uncontrolled approximation for which a priori estimates of the quality of the approximation are not available. For detailed accounts of real-space renormalization ideas applied to percolation and conduction, see Sahimi (2003a) and (chapter► “Scaling Theory of Percolation Clusters” by D. Stauffer in this Encyclopedia).

The effect of renormalization is to reduce the correlation length in the system, moving the system away from the percolation threshold. Sahimi et al. (1983c) have given an improved, though still uncontrolled approximation, in which

Conduction and Diffusion in Percolating Systems, Table 3 Estimates of the conductivity (t) and superconductivity (s) exponents in three dimensions. Several estimates of t obtained before 1984 that are very low compared to more modern estimates are not shown. Where values of t/v or s/v are given, these values were obtained first by finite-size scaling or related ideas, and the values of t or s were subsequently deduced. Neither v nor p_c are known exactly and estimates are sensitive to choices made by the cited authors. All estimates are for the simple cubic lattice bond problem, except for (i) the random walk estimate

t/v	v used	t	Source
2.095 ± 0.016	0.89 ± 0.01	1.867 ± 0.035	Finite-size scaling (Sahimi et al. 1983b)
2.21 ± 0.03			Lattice random walks with $p > p_c$ (Cen et al. 2012b)
2.26 ± 0.02			Molecular trajectory algorithm (Cen et al. 2012b)
2.26 ± 0.04			Special purpose computer (Normand and Herrmann 1995)
2.276 ± 0.012	0.88 ± 0.02	2.003 ± 0.047	Finite-size scaling (Gingold and Lobb 1990)
2.282 ± 0.005			Current distribution moments (Batrouni et al. 1996)
2.283 ± 0.003		2.00 ± 0.01	Two finite-size scaling methods (Kozlov and Lague's 2010)
2.288 ± 0.003			Finite size scaling (Li and Chou 2009)
2.305 ± 0.015	≈ 0.88	≈ 2.0	Finite-size scaling (Clerc et al. 2000)
		2.02 ± 0.02	Monte Carlo as $p \rightarrow p_c$ (Clerc et al. 2000)
≈ 2.315			Generalized transfer matrix (Byshkin and Turkin 2005)
2.32 ± 0.02			Lattice random walks at p_c (Cen et al. 2012b)
2.48 ± 0.07			Lattice random walks (Roman 1990)
s/v	v used	s	Source
0.782 ± 0.019			Finite-size scaling (Sahimi 1984)
0.85 ± 0.04	≈ 0.88	≈ 0.75	Transfer matrix (Herrmann et al. 1984)
0.835 ± 0.005			Special purpose computer (Normand and Herrmann 1990)

approximate renormalization is used to map the system to parameter values where the effective medium approximation is more accurate. This renormalized effective medium approximation effectively increases the interval in which the effective medium approximation works, but like all effective medium treatments cannot accurately portray the ultimate asymptotic behavior as $p \downarrow p_c$. An example of the resulting approximation is given in Fig. 2, together with the simple effective medium approximation (Kirkpatrick 1973), an alternative improved effective medium approximation (Ahmed and Blackman 1979) and simulation data (Kirkpatrick 1973). The reader should note from the simulation data, which the approximate curve of Sahimi et al. matches well except very close to the threshold, the clear nonlinear behavior of the conductivity, in striking contrast to the global linear behavior predicted by the simple effective medium theory and the ultimate

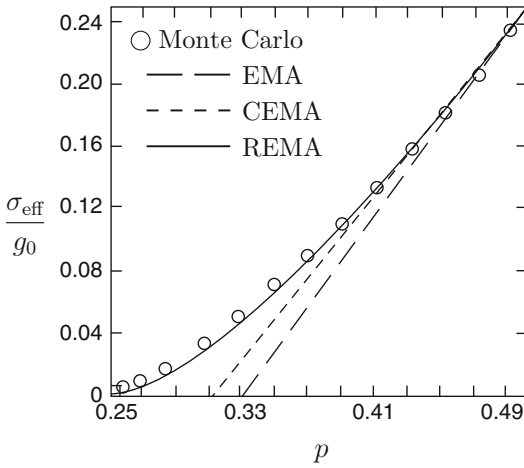
(Roman 1990) for the simple cubic lattice site problem; (ii) the molecular trajectory algorithm (Cen et al. 2012b); and (iii) three studies considering both site and bond problems – the special purpose computer transfer matrix calculation (Normand and Herrmann 1995); the Monte Carlo study (Kozlov and Lagues 2010) in which t and t/v were obtained independently by studying lattices of size L at occupancy p in the cases $p = p_c$, L variable and L fixed, p variable, respectively, and used to deduce that $v = 0.876 \pm 0.006$; and the separate finite-size scaling analyses of the site and bond problems (Li and Chou 2009)

linear behavior also predicted by the improved approximations near their predicted approximate percolation thresholds.

Numerical Estimates of the Conductivity Exponent t

Although it is possible to estimate the conductivity exponent t from an approximate determination of $\sigma_{\text{eff}}(p)$ on an interval including p_c , greater computational efficiency comes from the extension of the *finite-size scaling* ideas of Fisher (1971) to the percolation conduction problem (Clerc et al. 2000; Grassberger 1999; Lobb and Frank 1979; Mitescu et al. 1982; Sahimi et al. 1983b).

We explain the argument for the hypercubic lattice $\mathbb{Z}^d$, but the argument should apply for all periodic lattices. As the percolation threshold is approached, the correlation length $\xi(p)$ in the infinite lattice diverges:



Conduction and Diffusion in Percolating Systems, Fig. 2 Effective conductivity of the simple cubic lattice bond problem for the standard percolation conduction model (32). Monte Carlo simulation data (circles (Kirkpatrick 1973)) give clear evidence that the conductivity exponent t exceeds 1. The curves represent uncontrolled approximations: EMA, simple effective medium approximation (Kirkpatrick 1973); CEMA, cluster effective medium approximation (Ahmed and Blackman 1979); REMA, hybrid theory (renormalized effective medium approximation) (Sahimi et al. 1983c). (Figure reproduced with permission from Sahimi et al. (1983c))

$$\xi(p) \propto |p - p_c|^{-\nu}. \quad (60)$$

Although in principle the critical exponents for the correlation length for $p > p_c(v')$ and for $p < p_c(v)$ could differ, they have been proved rigorously to coincide for site percolation on the triangular lattice and there is no evidence to support their being different for other lattices. The argument is therefore written out in terms of ν .

Consider the finite hypercube $\Lambda_L \subset \mathbb{Z}^d$ introduced in section “Defining the Conductivity.” The finite lattice Λ_L will represent the infinite lattice to a good approximation provided that $\xi(p) \ll L$. We assume that the conductivity $\sigma_L(p)$ of the finite lattice depends on $|p - p_c|$ only through the ratio $\xi(p)/L \propto (L|p - p_c|^\nu)^{-1}$, and we write

$$\sigma_L(p) \approx L^{-\kappa} f(L|p - p_c|^\nu). \quad (61)$$

Since the conductivity is nonzero at $p = p_c$ for some realizations of the finite lattice, $f(0) \neq 0$. We assume that $f(u) \propto u^\lambda$ as $u \rightarrow \infty$ so that

$\sigma_L(p) \propto L^{-\kappa} [L|p - p_c|^\nu]^\lambda$. To recover the appropriate asymptotic law (44) for the conductivity of the infinite lattice, that is, $\sigma_{\text{eff}} \propto (p - p_c)^t$ as $p \rightarrow p_c^+$, we require $\lambda = \kappa$ (to cancel out the L -dependence), and to obtain the correct dependence on $p - p_c$, we need $t = \nu\lambda$. Hence,

$$\sigma_L(p) \approx L^{-t/\nu} f(L|p - p_c|^\nu) \quad (62)$$

and in particular

$$\sigma_L(p_c) \approx L^{-t/\nu} f(0). \quad (63)$$

The best available estimates of t come from the use of this asymptotic relation to determine t/ν and then using the exact value $\nu = \frac{4}{3}$ for $d = 2$ or independent numerical estimates of ν for $d \geq 3$.

In comparison with estimating the purely geometric or topological parameters of a percolation model, conductivity estimates are comparatively expensive in terms of computer time. There is a trade-off between having high precision in the values of the average conductivity of the finite lattice and having large enough L values to use the asymptotic relation (63). The most precise estimates of t/ν presently available come from Monte Carlo simulations, in which a random subset of the possible realizations of the lattice is generated for a sequence of values of L . Although the difference equations for the potential can be solved by standard techniques of numerical linear algebra, it is more efficient to perform a sequence of transformations that replace locally complicated small sections of the conducting backbone of the system by equivalent single bonds (Clerc et al. 2000; Grassberger 1999; Lobb and Frank 1979); this is especially effective in two dimensions. An alternative technique for two-dimensional systems can be devised using transfer matrices, with the conductivity of one realization of an infinite strip of width L being estimated for a sequence of values of L (Derrida and Vannimenus 1982; Derrida et al. 1984), and a generalization of this method that works in higher dimensions is also available (Byshkin and Turkin 2005; Herrmann et al. 1984). Other efficient methods of solving the relevant linear equations are also known (Knudsen and Fazekas 2006).

Finite-size scaling arguments also apply to the superconductivity problem in which a fraction p of the bonds have infinite conductance, and one finds that

$$\sigma_L(p_c) \propto L^{s/v} \text{ as } L \rightarrow \infty. \quad (64)$$

A selection of the better estimates for t/v and s/v and corresponding predictions for t and s are given in Table 2 ($d = 2$) and Table 3 ($d = 3$), together with a few estimates not derived via finite-size scaling (some based on random walk simulations). A number of plausible conjectures on relations between various exponents, based on heuristic arguments or phenomenological relations observed from early numerical estimates, are now comprehensively refuted (Hughes 1996; Grassberger 1999). Grassberger (1999) has carefully assessed the relative merits of different schemes for estimating t/v in two dimensions and notes major issues with the quality of random number generators used for some simulations, and problems arising from inappropriate assumptions concerning correction to scaling terms for the square lattice bond problem. The square lattice site problem, and the bond problems on the triangular and honeycomb lattices, are better behaved (Grassberger 1999; Reš 2001). Early estimates of t and s by finite-size scaling for lattices with unknown percolation thresholds are partly compromised by inaccuracy in numerical estimates of thresholds, but in some cases numerical estimates of thresholds are now available to extravagant precision (e.g., square lattice site problem, $p_c = 0.592746\,5 \pm 0.000000\,4$; simple cubic lattice site problem, $p_c = 0.311607\,7 \pm 0.000000\,4$ (Deng and Blöte 2005)).

A weak inequality relating the critical exponents t and v can be deduced on the basis of finite-size scaling. For finite fragments of the square lattice, a duality argument shows that there is probability $\frac{1}{2}$ that the fragment is spanned by a conducting path at $p = \frac{1}{2}$. Each such realization of the system gives a conductance between the connected sides of the lattice which is no smaller than aL^{-2} , this worst case arising when there is a single path passing through all lattice sites. It follows that for the square lattice, $\sigma_L(p_c) \geq (a/2)ML^{-2}$ and so $t \leq 2v$ in two dimensions.

Conduction on Fractals

Some progress has been made for percolation conduction problems on self-similar fractal structures (Mandelbrot 1982), which have been proposed as possible models for the backbone of large clusters at the percolation threshold (Gefen et al. 1981). The plane Sierpinski lattice (triangular gasket) has percolation threshold $p_c = 1$, but unlike the linear chain which also has $p_c = 1$, the Sierpinski lattice has nontrivial finite-size scaling behavior, and the analogue of t/v is $\log(5/3)/\log(2) \approx 0.73$ (Gefen et al. 1981). The analogue of s/v has been evaluated numerically for this system as 0.27 ± 0.03 (Taitelbaum and Havlin 1988). For a further discussion of fractal structures in the context of percolation, see chapter ► “Scaling Theory of Percolation Clusters” by D. Stauffer in this Encyclopedia.

Structural Speculations

Despite recent spectacular advances in the understanding of two-dimensional percolation mentioned in section “Rigorous Results for Two Dimensions,” an adequate theory for the conductivity exponent t and superconductivity exponent s remains elusive, even in two dimensions. A number of attempts have been made to model the structure of the backbone just above the percolation threshold, and to model what physicists have called the “incipient infinite cluster” at the percolation threshold p_c , in the hope of predicting the values of t , s and related “dynamical” exponents of percolating systems.

The Backbone

The backbone in a percolating system includes all sites with two independent connections to infinity. Only the backbone can carry current in the random resistor problem, although because of local symmetries, not all bonds of the backbone will carry nonzero current. On periodic lattices, the existence of a well-defined nonzero *backbone probability* $B(p)$ for $p > p_c$ ensures (as a consequence of ergodic theory (Billingsley 1965)) a well-defined density of backbone sites, and so the number $B_L(p)$ of sites with two disjoint connections to the boundary in a hypercube of side L is asymptotically a multiple of $L^d B(p)$ as

$L \rightarrow \infty$. Natural finite-size scaling analysis (Stauffer and Aharony 1994) (cf. section “**Numerical Estimates of the Conductivity Exponent t** ” above) based on the functional form

$$B_L(p) = L^\kappa b(L|p - p_c|^\nu)$$

with $b(z) \propto z^\lambda$ as $z \rightarrow \infty$ and the requirement that $B(p) \propto (p - p_c)^{\beta_{bb}}$ as $p \downarrow p_c$ leads to the conclusion that $d = \kappa + \lambda$ and $\beta_{bb} = \lambda\nu$. Thus, in particular, $B_L(p_c) \propto L^{d_{bb}}$, where $d_{bb} = d - \beta_{bb}/\nu$ is a formula believed to hold by physicists for $d \leq 6$, interpreted by them as the fractal dimension (Mandelbrot 1982) of the backbone at the percolation threshold, and estimated by simulation. Grassberger (1999) estimates that $d_{bb} = 1.6432 \pm 0.0008$ from a careful study of the square lattice site and bond percolation problems. The occurrence of this noninteger exponent suggests delicate structure of the backbone just above the percolation threshold.

The first attempts to model the backbone in detail and thereby make predictions about the conductivity exponent date from 1975 and 1976 and are due to de Gennes (1976b) and Skal and Shklovskii (1975). In their view, the backbone consisted of a “superlattice” of nodes connected by macrobonds or links. If the node spacing is estimated as $\xi(p)$, the correlation length, and the conductivity of a macrobond is given by $g(p) \propto (p - p_c)^\zeta$ for some exponent ζ , then the effective conductivity is predicted to scale as

$$\sigma_{\text{eff}}(p) \approx \xi(p)^{2-d} g(p) \propto (p - p_c)^{(d-2)\nu + \zeta}, \quad (65)$$

the factor of $\xi(p)^{2-d}$ being motivated by Eq. (39). This prediction implies that the conductivity exponent is $t = \nu(d - 2) + \zeta$, and it was suggested (de Gennes 1976b) that $\zeta = 1$ in all dimensions. However, Chayes and Chayes (1987) proved rigorously that $\zeta > \nu$ in all dimensions, implying that $t > \nu(d - 1)$. For $d = 2$, this gives $t > \frac{4}{3}$, a result which is no longer credible given the precision recently attained in numerical estimates and the simple superlattice model is unviable.

Problems with the superlattice model were already noted by Kirkpatrick (1978) in 1978. He proposed instead a self-similar fractal model, and this idea was further pursued by Gefen et al. (1981). An implication of the self-similar fractal model that $t \leq (d - 1)\nu$ is consistent with numerical data in low dimensions, but fails for $d = 6$, where it is accepted that $\nu = \frac{1}{2}$ and $t = 3$.

The most plausible picture of the backbone structure just above the percolation threshold is inelegantly described as the “nodes–links–blobs” model (Stanley 1977; Stanley and Coniglio 1983), with approximately self-similar structures over smallest scales linked together in some way by tortuous, quasi-one-dimensional links but the structure is far from completely characterized.

The Incipient Infinite Cluster

Since the percolation probability $P_\infty(p)$ is proven rigorously to be zero at the percolation threshold for several two-dimensional percolation problems, there is with probability 1 no infinite cluster present at the percolation threshold. The *incipient infinite cluster* at the percolation threshold in the sense originally used by physicists is therefore a dubious construct. Kesten has given a rigorous discussion of two mathematically respectable candidates for the incipient infinite cluster (Grimmett 1999; Kesten 1986b), using appropriately defined conditional probabilities.

- (i) Take $p > p_c$ and work with conditional probabilities, conditioning on the event that the origin is part of an infinite cluster. Then take the limit $p \downarrow p_c$.
- (ii) Take $p = p_c$ and work with conditional probabilities, conditioning on the event that the origin belongs to a connected cluster that reaches the boundary of a box of side length $2n$ centered on the origin. Then take the limit as $n \rightarrow \infty$.

For bond percolation on the square lattice, these two apparently different definitions have been proved consistent (Kesten 1986b). Moreover, for this specific problem, it can be shown that the expected number of sites of the incipient infinite cluster in a

box of side $2n$ is (to within a slowly-varying prefactor) $n^{2-\eta}$, where the exponent η governs the decay of the probability that the origin is connected to a box of side $2n$. It has been proved that for the triangular lattice bond problem, $\eta = \frac{5}{24}$ (Smirnov and Werner 2001), and this should be generally true for two dimensions. In physicists' terminology, this shows that the fractal dimension of the incipient infinite cluster in two dimensions is $d_{\text{iiic}} = \frac{43}{24} \approx 1.792$, which is outside the 1983 estimates $d_{\text{iiic}} = 1.90 \pm 0.1$ (Puech and Rammal 1983) and $d_{\text{iiic}} = 1.900 \pm 0.009$ (Kapitulnik et al. 1983).

The theory of the incipient infinite cluster and its relation to finite-size scaling considerations are completely resolved in two dimensions (Borgs et al. 2001; Járai 2003). Some illuminating if less complete conclusions are available in higher dimensions (Borgs et al. 2001). Physicists' scaling theories suggest that $d_{\text{iiic}} = d - \beta/\nu$ for $2 \leq d \leq 6$ (Stauffer and Aharony 1994). However, it is not the incipient infinite cluster but rather the backbone that is core to the determination of the conductivity exponent, so that these results do not go far enough for the present purposes.

Random Motion in a Random Environment

One may replace the steady-state transport and conduction processes discussed in sections “[Continuum Models: Steady-State Phenomena](#)” and “[Lattice Models: Steady-State Phenomena](#)” for continua and lattices, respectively, by time-dependent analogues. Our discussion of the continuum version is very brief.

Continuum Problems

The most natural model of random motion in a random continuous medium to study is the diffusion equation (5), with the diffusivity D a random function of position, subject to some requirement of probabilistic translational invariance or ergodicity. Early studies (Kozlov 1978; Papanicolaou and Varadhan 1982a) considered a more general locally anisotropic problem with the diffusive flux $-D \nabla c$ replaced by $-D \cdot \nabla c$, where D is a randomly spatially varying diffusivity tensor.

They essentially established the problem's equivalence under homogenization to diffusion with a uniform diffusivity (or diffusivity tensor), subject to the random diffusivity D being both bounded above and bounded below by a positive constant (or the random diffusivity tensor constrained so that for all constant vectors ξ we have $k|\xi|^2 \leq \xi \cdot D \cdot \xi \leq K|\xi|^2$, where k and K are positive constants). These constraints (a uniform ellipticity condition) parallel similar constraints for well-understood homogenization in steady state continuum problems. Provided that the diffusivity (or diffusivity tensor) is stationary in the probabilistic sense and uniform ellipticity applies, the system can be homogenized for almost all realizations of the random diffusivity distribution, and the corresponding homogenized diffusivity is independent of the realization (Jikov et al. 1994). Similar conclusions are found (Papanicolaou and Varadhan 1982b) under the same restrictions on D or D when

$$\nabla \cdot (D \nabla c) \text{ or } \nabla \cdot (D \cdot \nabla c) = \sum_{i=1}^d \frac{\partial}{\partial x_i} \sum_{j=1}^d D_{ij} \frac{\partial c}{\partial x_j}$$

are replaced by

$$D \nabla^2 c \text{ or } \sum_{i=1}^d \sum_{j=1}^d D_{ij} \frac{\partial^2 c}{\partial x_i \partial x_j},$$

respectively.

The uniform ellipticity restriction excludes the possibility of percolation phenomena. Jikov et al. (1994) give a proof that for the random chessboard (squares with diffusivities 0 or 1 with probabilities $1-p$ and p , respectively), the scaled displacement $\mathbf{X}(t)$ of a diffusion process commencing in the conducting phase converges in distribution to a zero mean, isotropic bivariate normal random variable. If D_0 denotes the homogenized diffusivity for the steady-state problem treated like a steady conduction problem, then the diffusivity governing the time-dependent problem is $D_0/P_\infty(p)$, where $P_\infty(p)$ is the density of the infinite conducting cluster (and indeed equal to the percolation probability for site percolation on the square lattice).

For a discussion of many aspects and applications of diffusion in condensed matter physics, an area that has sustained interest in the properties of heterogeneous and randomly microstructured materials for a long time, see the collection edited by Heitjans and Kärger (2005). One interesting diffusion problem that we do not address, since it does not manifest percolation properties, arises when one phase acts as an irreversible trap. The survival probability for diffusing objects in the presence of dilute random traps decays as $\exp(-kt^{3/5})$ at large times t in three dimensions rather than the naively expected $\exp(-kt)$, due to the unexpected statistical importance of rare, large trap-free regions (Grassberger and Procaccia 1982; Hughes 1995; Kayser and Hubbard 1983).

Lattice Problems

The lattice-based models for stochastic transport processes in random environments that we address may loosely be described as *random walks*, since they derive conceptually from the random walk problems first posed in 1905 by Pearson (1905) and in 1919 by Pólya (1919, 1921), but the precise meaning of the phrase *random walk* varies widely in the literature. The classic account of the traditional theory of discrete time, translationally invariant random walks on $\mathbb{Z}^d$ is Spitzer (1976); substantial extensions to the theory needed for more general problems will be found in Barlow (2017), Doyle and Snell (1984), Hughes (1995, 1996), Lawler and Limic (2010), Telcs (2006), and Woess (2000). The most recent comprehensive rigorous reviews of random walks in random environments are the papers by Varadhan (2004) and Zeitouni (2004, 2006). For other reviews or expository accounts of random walks in random environments, see the books by Hughes (1996), Kumagai (2014a), and Révész (2013), and the papers by Bogachev (2006), Kumagai (2014b), and Sznitman (Sznitman 2004, 2006).

We shall only consider the case in which the random environment that controls the probabilities of stepping between nearest-neighbor sites is constant in time, although we note that there have been a number of studies of time-varying random environments: see, for example, Andres (2014),

Andres et al. (2018), Bandyopadhyay and Zeitouni (2006), Boldrighini et al. (2004), Rassoul-Agha and Seppäläinen (2005), and Redig and Völlering (2013).

For stochastic transport in random environments, where we have both spatial disorder in the environment (which does not change with time) and the walker's random motion, it is necessary to distinguish carefully between results about the random walk that apply to an arbitrary specific realization of the environment (usually called the *quenched* case) and results which hold averaged over all possible realizations of the environment (usually called the *annealed* case).

Nearest-Neighbor Stepping Discrete-Time Random Walk

We consider the case in which the probability that a walker presently at site $\mathbf{s}'$ next steps to site $\mathbf{s}$ is $p(\mathbf{s}|\mathbf{s}')$, nonzero only when $\mathbf{s}$ is a nearest neighbor of $\mathbf{s}'$. The site occupancy probability $p_n(\mathbf{s}|\mathbf{s}_0)$ after n steps for a walk starting from site $\mathbf{s}_0$ is governed by the equation

$$p_{n+1}(\mathbf{s}|\mathbf{s}_0) = \sum_{\mathbf{s}'} p(\mathbf{s}|\mathbf{s}') p_n(\mathbf{s}'|\mathbf{s}_0), \quad (66)$$

to be solved with the initial condition $p_0(\mathbf{s}|\mathbf{s}_0) = \delta_{\mathbf{s},\mathbf{s}_0}$. The walk is called *recurrent* if there is probability 1 that the walker eventually returns to the starting site and *transient* otherwise. A recurrent walker is certain to visit all sites accessible to it and visits its own starting site infinitely often (with probability 1). A transient walker revisits the starting site at most finitely many times.

The walk is of Pólya type if $p(\mathbf{s}|\mathbf{s}') = 1/z(\mathbf{s}')$, where $z(\mathbf{s}')$ is the coordination number of $\mathbf{s}'$, that is, all nearest-neighbor steps are equally likely. Pólya's most famous result is that for Pólya walk on $\mathbb{Z}^d$, the walk is recurrent for $d = 1$ and $d = 2$, but transient for $d \geq 3$. Translationally invariant walks are well-suited to Fourier analysis. This is how much of the classical theory is derived, and the discrete time evolution is simplified by generating function methods (Hughes 1995; Spitzer 1976). In particular, for Pólya walks on $\mathbb{Z}^d$, the probability $p_n(\mathbf{s}_0|\mathbf{s}_0)$ that the walker will be found at the starting site $\mathbf{s}_0$ after n steps decays in

proportion to $n^{-d/2}$ and the position distribution of the random walker is asymptotically Gaussian (normal) at large times. Expressed slightly informally, if we identify the unit spacing between nearest-neighbor sites on $\mathbb{Z}^d$ with a length scale Δ , introduce a time τ between successive steps and write $p_n(\mathbf{s}_0 + \mathbf{l} | \mathbf{s}_0) = \Delta^{-d} c(\Delta \mathbf{l}, n\tau)$, then in the joint limit $\Delta \rightarrow 0$ and $\tau \rightarrow 0$ with $D = \Delta^2/(2d\tau)$ held constant, we recover the diffusion equation (5) for the time evolution of $c(\mathbf{r}, t)$, and its fundamental solution

$$c(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{|\mathbf{r}|^2}{4Dt}\right), \quad (67)$$

corresponding to the initial condition $c(\mathbf{r}, 0) = \delta(\mathbf{r})$. These results hold quite generally for translationally invariant random walks on $\mathbb{Z}^d$, provided that the mean-square displacement per step is finite (always the case with nearest-neighbor stepping, to which the present discussion is restricted) and the mean displacement per step is zero, though in this more general case the multi-dimensional Gaussian distribution need not be isotropic, and $|\mathbf{r}|^2/(4D)$ inside the exponential is replaced by a positive-definite quadratic form.

The number S_n of distinct sites visited in the first n steps is of interest in a number of contexts (Hughes 1995); in the probability literature, this quantity is sometimes misleadingly called the range of the random walk. For classical Pólya walks on $\mathbb{Z}^d$, the mean number of distinct sites visited has the asymptotic behavior (Montroll and Weiss 1965).

$$\langle S_n \rangle \sim \begin{cases} (8n/\pi)^{1/2}, & d = 1, \\ \pi n / \ln n, & d = 2, \\ (1 - R)n, & d \geq 3, \end{cases} \quad (68)$$

where R is the probability of eventual return to the starting site. The following more general results hold (Hughes 1995) for translationally invariant walks on periodic lattices. For transient walks, $\langle S_n \rangle \sim (1 - R)n$. For recurrent walks, if $p_n(\mathbf{s}_0) \sim \text{constant} \times n^{-H/2}$ with $0 < H < 2$, or equivalently,

$$\sum_{n=0}^{\infty} p_n(\mathbf{s}_0) \xi^n \sim \text{constant} \times (1 - \xi)^{H/2-1} \text{ as } \xi \uparrow 1, \quad (69)$$

then

$$\langle S_n \rangle \sim \text{constant} \times n^{H/2}. \quad (70)$$

(For walks of Pólya type on $\mathbb{Z}^d$, and other walks in which return to the start is possible only on an even-numbered step, one has to be more careful and say that $p_{2n}(\mathbf{s}_0) \sim \text{constant} \times n^{-H/2}$.) The exponent H is variously described as the *harmonic dimension* (Hughes 1995), *spectral dimension* or *fractal dimension* (Alexander and Orbach 1982). We may take $p_{2n}(\mathbf{s}_0) \sim \text{constant} \times n^{-H/2}$ as the definition of the harmonic dimension if we wish to extend our discussion to recurrent walks, leading to $\langle S_n \rangle \sim \text{constant} \times n^{-\min(H/2, 1)}$, typically with a logarithmic prefactor needed when $H = 2$. For Pólya walks on $\mathbb{Z}^d$, $H = d$.

For random walk problems where the generating function and Fourier analysis techniques used to derive the preceding results are not available, the important questions to be addressed in other ways are as follows.

- (i) Is the walk recurrent or transient?
- (ii) Is the walk diffusive (large- n Gaussian or normal limiting behavior) and if so, what is the value of diffusion constant?
- (iii) In nondiffusive cases, how does the mean-square displacement grow with n ?
- (iv) What is the value of the harmonic dimension?

A simple scaling argument (Hughes 1995) due originally to Alexander and Orbach (1982) suggests that $H = 2d_f/d_w$ quite generally, where d_f is the fractal dimension of the lattice and the mean-square displacement of an n -step random walk on the lattices is $\langle R_n^2 \rangle^{1/2} \propto n^{1/d_w}$ as $n \rightarrow \infty$. This scaling law, true for translationally invariant systems and at least some fractals, is problematic for some pseudolattices (Haynes and Roberts 2009;

Nakanishi and Herrmann 1993). In studying question (iii), it is natural to address also the first exit time from a ball of large radius when the walker starts at the center of the ball. The distance used to define the radius of the ball may be either the normal Euclidean distance between sites, or the graphical distance.

In the context of question (ii) above, for walks on $\mathbb{Z}^d$ it is natural to seek upper and lower bounds for distribution of the walker's position in the lattice-based process that mimics the fundamental solution (67) of the diffusion equation problem (5) with constant diffusivity D in $\mathbb{R}^d$. Since the diffusion equation is more commonly referred to as the heat equation in the partial differential equations literature, bounds that resemble the right-hand side of Eq. (67) are often called heat kernel bounds.

Comparison against the continuum diffusion solution (67) is not appropriate if the environment imposes a systematic drift that leads to a nonzero mean velocity, which some authors describe as the ballistic case. One way to avoid the ballistic case for walks on $\mathbb{Z}^d$ is to require the random environment to be balanced, in the sense that that for each site, the probabilities that a walker arriving there next increases a particular coordinate by 1 or decreases that coordinate by 1 are equal. Let $\mathbf{X}_n$ denote the position of the walker after n steps. A realization of a balanced random environment in which the walk takes place is an assignment of a vector $\varpi(\mathbf{s}) = (\varpi_1(\mathbf{s}), \dots, \varpi_d(\mathbf{s}))$ to each site $\mathbf{s}$, with $\varpi_i(\mathbf{s}) \geq 0$ and $\sum_{i=1}^d \varpi_i(\mathbf{s}) = 1$, such that if $\mathbf{e}_i$ is the unit vector in the i th coordinate direction,

$$\begin{aligned} \Pr\{\mathbf{X}_n = \mathbf{s} + \mathbf{e}_i | \mathbf{X}_{n-1} = \mathbf{s}\} \\ = \Pr\{\mathbf{X}_n = \mathbf{s} - \mathbf{e}_i | \mathbf{X}_{n-1} = \mathbf{s}\} = \frac{\varpi_i(\mathbf{s})}{2}. \end{aligned} \quad (71)$$

Let $\lfloor x \rfloor$ denote the largest integer no greater than x . Lawler (1982) established that for a stationary, ergodic distribution of the random vectors $\varpi(\mathbf{s})$, then for almost all environments, $n^{-1/2} \mathbf{X}_{\lfloor nt \rfloor}$ converges in distribution as $n \rightarrow \infty$ to d -dimensional Brownian motion with well-defined diagonal variance matrix. That is, the continuum limit of the process is (possibly anisotropic) diffusion. For stronger results than

Lawler's see Guo and Zeitouni (2012), Stenlund (2013) and Berger and Deuschel (2014). For example, the walk in a balanced environment is transient if $d \geq 3$ (Guo and Zeitouni 2012). Other aspects of the balanced random environment problem have been addressed, including exit times from large balls, typically under the additional assumption that $|\varpi_i(\mathbf{s}) - 1/(2d)|$ is kept sufficiently small (Baur 2013, 2016; Baur and Bolthausen 2015; Bolthausen and Zeitouni 2007).

Somewhat stronger results than those generally available have been found for discrete-time random walks on $\mathbb{Z}^d$ when the joint distribution of the $2d$ random variables $p(\mathbf{s}' | \mathbf{s})$ associated with a site $\mathbf{s}$ and its $2d$ nearest-neighbors $\mathbf{s}'$ is a Dirichlet law (Enriquez and Sabot 2006; Sabot 2011, 2013; Sabot and Tournier 2011). There are also some better results in the special case of a random walk in a random environment (in the random master equation formalism) for which the transition rates satisfy a divergence-free condition (Kozma and Tóth 2017; Tóth 2018). Some interesting results for two and three dimensions concerning large deviations, including differences between annealed and quenched large deviations estimates, have been discussed by Yilmaz and Zeitouni (2010). They do not require a balanced environment, but the transition probabilities are required to have a positive lower bound. All of these restricted models exclude the possibility of any kind of percolation threshold behavior.

For a discussion of the ballistic case including conditions for existence of a motion with a well-defined effective drift velocity about which the walker makes asymptotically Gaussian fluctuations in an appropriate limit, see Sznitman (2001, 2002, 2003). For a discussion of the rate of convergence to the drift velocity, see Berger (2012). Conditions under which (averaged over all realizations of the environment) the displacement $\mathbf{X}_n \in \mathbb{Z}^d$ satisfies a zero-one law for every vector direction $\mathbf{k}$, in the sense that

$$\Pr\{[\mathbf{X}_n \cdot \mathbf{k} \rightarrow \infty] \cup [\mathbf{X}_n \cdot \mathbf{k} \rightarrow -\infty]\} \in \{0, 1\},$$

and related results have been discussed by Kalikow (1981), Zerner and Merkel (2001) and Zerner (2007a, b).

Most of the result that we have described above are uninformative about random walks in random environments for which the transition probabilities for steps to nearest-neighbor sites can vanish, leading to the possibilities of the walker being trapped on a finite fragment of the lattice, or making excursions into large lattice fragments with few exit points, leading to long intervals of effective confinement. We shall address such environments shortly, after some remarks about continuous-time models for random walks on lattice-based random environments.

Continuous-Time Random Walk, Master, and Generalized Master Equations
Differential-difference equations of the form

$$\frac{d}{dt}c(s, t) = \sum_{s'} W(s, s')c(s', t) - M(s)c(s, t) \quad (72)$$

describe a process in which the concentration of a mobile substance at site s evolves by transfer of substance from other sites (gaining substance at rate $W(s, s')c(s', t)$ from site s') and loss of substance to other sites (total rate of loss $M(s)c(s, t)$ to all other sites). If the substance is to be globally conserved, one needs

$$M(s) = \sum_{s'} W(s', s) \quad (73)$$

and if we place all of the mass at site s_0 at time $t = 0$, and

$$p(s|s_0, t) = \frac{c(s, t)}{\sum_{s'} c(s', t)} \quad (74)$$

denotes the normalized concentration, then what physicists call the *master equation* (Oppenheim et al. 1977),

$$\frac{d}{dt}p(s|s_0, t) = \sum_{s'} [W(s, s')p(s'|s_0, t) - W(s', s)p(s|s_0, t)], \quad (75)$$

results. This equation is interpreted as the evolution equation for the probability distribution of the position at time t for a type of random walk process in continuous time and indeed is a standard equation from the theory of Markov processes.

To obtain a richer class of possible behaviors, physicists have also considered *generalized master equations* (Kenkre 1982), where the transition rates $W(s, s')$ are replaced by memory kernels $W(s, s', t)$:

$$\frac{d}{dt}p(s|s_0, t) = \int_0^t \sum_{s'} [W(s, s', t-t')p(s'|s_0, t') - W(s', s, t-t')p(s|s_0, t')]dt'. \quad (76)$$

Generalized master equations with separable memory kernels

$$W(s, s', t) = \phi(t)p(s|s') \quad (77)$$

are naturally associated with continuous-time random walk processes in which the walker waits for a random time with probability density function $\psi(t)$ between successive steps, and then moves with the stepping law $p(s|s')$. The classic exponential waiting time density $\psi(t) = \kappa \exp(-\kappa t)$ arises if and only if $\phi(t) = \kappa \delta_+(t)$ and the generalized master equation reduces to the ordinary master

equation in this case. In general, the connection between ϕ and ψ is most simply expressed in terms of their Laplace transforms $\hat{\phi}$ and $\hat{\psi}$ (Hughes 1995; Kenkre et al. 1973):

$$\hat{\psi}(u) = \hat{\phi}(u) / [u + \hat{\phi}(u)]. \quad (78)$$

Lattice-based studies of random walk processes may be pursued within either discrete-time or continuous-time contexts. Provided that the waiting-time density $\phi(t)$ has the simple exponential form $\psi(t) = \kappa \exp(-\kappa t)$, the probability

that precisely n steps occur between time 0 and the current time t is given by $(\kappa t)^n \exp(-\kappa t)/n!$ from the elementary theory of Poisson processes and we have a very simple relationship between the solution $p(\mathbf{s}|\mathbf{s}_0, t)$ of the continuous-time random walk problem and the discrete-time walk with the same transition probability, namely

$$p(\mathbf{s}|\mathbf{s}_0, t) = \sum_{n=0}^{\infty} p_n(\mathbf{s}|\mathbf{s}_0) \frac{(\kappa t)^n}{n!} \exp(-\kappa t). \quad (79)$$

Therefore, any reasonably strong conclusions able to be drawn about one of the discrete-time system or the continuous-time system will be informative for the other. However, in continuous-time formulations of the problem in which the waiting-time distribution at sites depends on the site, the relations between the discrete-time and continuous-time problems are generally less transparent.

Conductance-Based Models

Random environments for random walkers to experience may be constructed in various ways. Many of the results we have discussed above, although sometimes more widely applicable, pertain to the case in which the transition probabilities for nearest-neighbor steps away from a site $\mathbf{s}$ are assigned independently of the transition probabilities for steps away from other sites. In some sense in such models the environment disorder is naturally viewed as associated with individual sites and if we were to allow for some nearest-neighbor step choices to have zero probability in a realization of the environment, it would be quite natural to have $p(\mathbf{s}|\mathbf{s}') = 0$ but $p(\mathbf{s}'|\mathbf{s}) \neq 0$ for some pairs of nearest-neighbor sites $\mathbf{s}$ and $\mathbf{s}'$. In contrast, if we seek to model random walk in a lattice in which bonds become blocked to passage in both directions, then it is more natural to associate disorder in the environment with bonds rather than sites.

A simple way to embody bond-level disorder is to assign to each bond of the lattice $\mathbb{Z}^d$ (or some other periodic lattice) an independent nonzero weight, which might be interpreted as the conductance of a random resistor. If $G_{\mathbf{r},\mathbf{s}} = G_{\mathbf{s},\mathbf{r}}$ denotes

the conductance of a bond joining nearest-neighbor sites $\mathbf{r}$ and $\mathbf{s}$, then the transition probability may be defined to be

$$p(\mathbf{s}|\mathbf{s}') = \frac{G_{\mathbf{s},\mathbf{s}'}}{\sum_{\mathbf{s}''} G_{\mathbf{s}'',\mathbf{s}'}} \quad (80)$$

the sum over $\mathbf{s}''$ being restricted to nearest neighbors of $\mathbf{s}'$. If all bonds emanating from a given site have equal conductance, the walk is of Pólya type.

Consider the following two problems on the infinite conducting lattice just introduced:

- (i) a discrete-time random walk, governed by (80) starting from site $\mathbf{s}_0$.
- (ii) electrical conduction between site $\mathbf{s}_0$ and infinity.

Then it can be shown (Doyle and Snell 1984) that the walk is transient if and only if the total resistance between $\mathbf{s}_0$ and infinity is finite. This result, and various other relations between random walks and electric networks (Doyle and Snell 1984; Hughes 1996; Nash-Williams 1959), represents one of the most important avenues for progress in the study of random walks in random environments.

Pemantle and Peres (1996) have shown that for independent, identically distributed conductances, the question of recurrence or transience of this model can be settled (for all realizations of the environment save for a set of zero probability) by an analysis of Pólya random walk on the random lattice arising from the bond percolation model on the same lattice. The original walk is transient if and only if for some p with $p_c < p < 1$ the Pólya walk on the infinite cluster in the bond percolation problem is transient.

Some subtle possibilities are perhaps more clearly revealed when we consider models with continuous time evolution. For Eqs. (75) and (76), the transition rates or memory kernels are often nonzero only for nearest-neighbor sites. Simple models of random media arise by imposing symmetry,

$$W(\mathbf{s}, \mathbf{s}') = W(\mathbf{s}', \mathbf{s}) \text{ or } W(\mathbf{s}, \mathbf{s}', t) = W(\mathbf{s}', \mathbf{s}, t),$$

and making the rate coefficients $W(\mathbf{s}, \mathbf{s}')$ or parameters in the memory kernels $W(\mathbf{s}, \mathbf{s}', t)$

independent random variables. If we introduce Laplace transforms, writing

$$\hat{f}(u) = \int_0^\infty e^{-ut} f(t) dt, \quad (81)$$

then the transformed master and generalized master equations for a process started at the origin site $\mathbf{0}$ become

$$\begin{aligned} u\hat{p}(\mathbf{s}, u) - \delta_{\mathbf{s}, \mathbf{0}} &= \sum_{\mathbf{s}'} W(\mathbf{s}, \mathbf{s}') \\ &\times [\hat{p}(\mathbf{s}', u) - \hat{p}(\mathbf{s}, u)], \quad (82) \\ u\hat{p}(\mathbf{s}, u) - \delta_{\mathbf{s}, \mathbf{0}} &= \sum_{\mathbf{s}'} \hat{W}(\mathbf{s}, \mathbf{s}', u) \\ &\times [\hat{p}(\mathbf{s}', u) - \hat{p}(\mathbf{s}, u)]. \quad (83) \end{aligned}$$

In both cases, the Laplace transform equations are able to be interpreted as the equations governing a random resistor network, with all sites having an additional connection to zero potential (an earth connection) of conductance u . If we attempt to match Eq. (82), with random rates $W(\mathbf{s}, \mathbf{s}')$, to an equivalent uniform system with rates W_* , then it should be anticipated that W_* is a function of the variable u , since the relative importance of the earth connection at $\mathbf{s}$ compared to its connections to other sites will fluctuate over the lattice. Consequently, as discussed in section “Exactly and Approximately Solved Continuous-Time Problems,” the appropriate real-time description of the system may be expected to correspond to a uniform memory kernel generalized master equation, rather than a simple, uniform transition rate master equation.

A large amount of rigorous work on random walks in random environments is based on continuous-time walks related to the transition probabilities defined by Eq. (80), based on (symmetric) bond conductances $G_{\mathbf{s}', \mathbf{s}} = G_{\mathbf{s}, \mathbf{s}'}$. If we write

$$G_{\mathbf{s}} = \sum_{\mathbf{s}'} G_{\mathbf{s}', \mathbf{s}} \quad (84)$$

for brevity and take the transition rate parameter κ to be unity in a separable continuous-time walk

with the same exponential waiting-time density at all sites, we arrive at the master equation

$$\frac{d}{dt} p(\mathbf{s}|\mathbf{s}_0, t) = \sum_{\mathbf{s}'} G_{\mathbf{s}, \mathbf{s}'} \left[\frac{p(\mathbf{s}'|\mathbf{s}_0, t)}{G_{\mathbf{s}'}} - \frac{p(\mathbf{s}|\mathbf{s}_0, t)}{G_{\mathbf{s}}} \right]. \quad (85)$$

This model is sometimes referred to as a constant speed random walk among conductances (Kumagai 2014a). One may also consider the simpler-looking master equation

$$\frac{d}{dt} p(\mathbf{s}|\mathbf{s}_0, t) = \sum_{\mathbf{s}'} G_{\mathbf{s}, \mathbf{s}'} [p(\mathbf{s}'|\mathbf{s}_0, t) - p(\mathbf{s}|\mathbf{s}_0, t)]. \quad (86)$$

For this model, sometimes called the variable speed random walk among conductances (Kumagai 2014a), the choice of site $\mathbf{s}$ to step to from site $\mathbf{s}'$ is still governed by the transition probability (80), but now the waiting time to make a step from site $\mathbf{s}$ to a nearest-neighbor site is exponential with rate $G_{\mathbf{s}}$ rather than rate 1. The model (86) avoids some awkwardness that arises if a bond has zero conductance with finite probability.

For a review of what is known about both forms of the random conductance model, see Kumagai (2014a) and the more recent results of Barlow et al. (2015, 2016). Many studies (e.g., the central limit theorem results in Mourrat (2012) associated with the variable speed case) impose bounds of the form $0 < k \leq G_{\mathbf{s}, \mathbf{s}'} \leq K < \infty$, excluding both percolation phenomena and unboundedly rapid stepping, but some results for conductance distributions with an unbounded support and an infinite mean have been provided by Barlow and Černý (2011) for $d \geq 3$ and by Barlow and Deuschel (2010) for $d \geq 2$.

Exactly Solved Discrete-Time Problems

Elegant exact results are scarce for random processes in random environments, with the strongest and most informative results limited to one dimension (i.e., on $\mathbb{Z}$), where percolative problems become essentially trivial: for $p < 1$ a Pólya walker is confined to a finite interval and

essentially its position has a limiting distribution (to be more precise, the positions after even or odd numbers of steps have limiting distributions, which may be different). Averaging over all realizations of the environment we find that the mean-square displacement after n steps is $o(n)$. This unusual behavior is an artifact of averaging: as n increases, in more and more realizations the walker's displacements have saturated and only the effects of increasingly rare large intervals contribute to the continued growth of the mean-square displacement, and various properties of the system can be deduced by appropriate averaging over the positions of the left and right boundary sites (Odagaki and Lax 1980).

A less trivial one-dimensional model introduced by Temkin (1972) brings out the subtle possibilities for random walks in random environments. Consider the stepping law

$$p(l|l') = A_l \delta_{l,l'+1} + (1 - A_l) \delta_{l,l'-1}, \quad (87)$$

where $\{A_l\}$ is a set of independent, identically distributed random variables. Let an overbar denote an average over all realizations of the set $\{A_l\}$. Solomon (1975) has shown that: a walker initially stepping right is certain to return if and only if $\log[(1 - A)/A] \geq 0$; a walker initially stepping left is certain to return if and only if $\log[A/(1 - A)] \geq 0$, and the walk is recurrent if and only if $\log[A/(1 - A)] = 0$. Goldsheid (2007) has discussed the sufficient conditions for the Central Limit Theorem (Gaussian long-time limiting behavior) for the transient case of Temkin's model. Temkin's model may be generalized to give the walker the option to pause at the current site on any step: for simulations of this extended model, see Simula and Stenlund (2010). In random walk theory generally, a walk model is called strongly transient if it is transient (so not all walks return to the starting site), but conditioned on the walker returning to the starting site, the mean time to return is finite. Peterson (2015) has analyzed conditions for strong transience in Temkin's model. Comets et al. (2000) have given results on large deviations from the average behavior in Temkin's model.

Sinai (1982) produced the astonishing result that in the recurrent case, on the additional assumption that A_l is bounded away from 0 and 1, the mean-square displacement is $O(\ln^4 n)$, in place of the standard $O(n)$ for one-dimensional Pólya walkers. An alternative derivation of slightly stronger results than Sinai's under weaker hypotheses has been given by Andreolotti (2005). The limiting distribution for Sinai's random walk has been determined by Kesten (1986a). For bounds on maximum displacements reached, numbers of returns to the origin, the probability of displacements somewhat larger than the root-mean-square displacement, the location of the most often visited site, and other attributes of Sinai's walk, see Deheuvels and Révész (1986), Hu and Shi (1998, 2000), and Comets and Popov (2003, 2004). Cheliotis and Virág (2013) have established that some interesting patterns appear in Sinai's walk on exponential time scales.

The origin of the anomalous behavior of the displacement in Sinai's problem is the existence of temporary traps (intervals which it is easy for the walker to enter but hard to leave). The longer the time for which the walker has been in motion, the more likely it is to encounter such traps, and the longer the typical holding time in the hardest-to-leave trap so far encountered will be, and some quantification of the holding times is available (Dolgopyat and Goldsheid 2012). Temporary trapping in hard-to-leave regions can also occur in higher-dimensional cases, though the effects are not typically as extreme as in Sinai's one-dimensional example (Bogachev 2006; Sznitman 2004, 2006).

Exactly and Approximately Solved Continuous-Time Problems

Alexander et al. (1981) discussed exactly solvable one-dimensional master equations with independent, identically distributed random transition rates in an early pioneering study of what has been described above as the variable speed random conductance model. If the probability density function for the rates is denoted by $f(w)$, they show that the mean-square displacement grows as $2W_0 t$, and the random system is equivalent in its

long-time properties to a uniform system in which all transition rates are W_0 , where

$$\frac{1}{W_0} = \int_0^\infty \frac{f(w)dw}{w}, \quad (88)$$

so long as the integral on the right is finite. When this is not the case, the random motion is *subdiffusive*: if $f(w) \rightarrow f(0) > 0$ as $w \rightarrow 0$ then the mean-square displacement grows as $t/\ln t$, while if $f(w) \propto w^{-\alpha}$ as $w \rightarrow 0$ the mean-square displacement grows as $t^{(2-2\alpha)/(2-\alpha)}$ (distribution-induced nonuniversality). There are several of other approaches to exactly solvable one-dimensional master equation problems, including asymmetric random walk problems (Hughes 1996).

A number of authors have extended the idea of an effective medium approximation from the random resistor problem (section “[Effective Medium Approximations](#)”) or other contexts to the problem of random master equations. For historical details and a full account of the analysis, see Sahimi et al. (1983a) or Hughes (1995). As noted in section “[Continuous-Time Random Walk, Master, and Generalized Master Equations](#),” in the Laplace transform domain, the master equation with random coefficients is equivalent to a random resistor network, and the uniform transition rate produced by the matching procedure is a function of the transform variable, so that the approximately equivalent uniform system is governed by a generalized master equation. In the percolative case in which the rate coefficient associated with a bond is nonzero only with probability $p < 1$, the approximately equivalent uniform system does not support motion if $p < 2/z$ (the predicted percolation threshold, where z is the coordination number of the underlying lattice on which the percolation process is realized). For $p \downarrow 2/z$, the effective diffusion constant $D(p)$ (a constant multiple of the time derivative of the mean-square displacement) is predicted to vanish linearly with $p - 2/z$ for the standard case where all nonzero rate coefficients are equal, but the exponent is predicted to change in more general cases if the average of W^{-1} is infinite, where W is the random rate associated with an arbitrary bond, conditional on the rate being nonzero.

In one dimension, the effective medium approximation reproduces a number of the exact results of Alexander et al. (1981). Its predictions for higher-dimensional systems, while not of great accuracy, do have one interesting aspect. Any form of nondiffusive behavior that may arise is naturally associated with a nonexponential waiting time density, and for $p < 2/z \approx p_c$ the associated waiting time is predicted to be defective, that is,

$$\int_0^\infty \psi(t)dt < 1 \quad (89)$$

and the equivalent continuous time random walker takes only finitely many steps. An alternative approach to modeling nondiffusive behavior of possible relevance to percolative systems can be developed using fractional calculus ideas (Metzler and Klafter 2000, 2004).

The Ant in the Labyrinth

We conclude our survey of transport and conduction in random environments, with a discussion for discrete-random walks of the problem of the ant in the labyrinth, introduced by Brandt (1975) and proposed by de Gennes (1976a) as a probe of the geometry of percolation. The ant, a random walker, moves through a random labyrinth generated by applying site or bond percolation to a periodic lattice (Brandt 1975; de Gennes 1976a; Hughes 1996; Mitescu and Rousseny 1976, 1983; Mitescu et al. 1978). Because the analogue of a strong ellipticity condition is not satisfied for these percolative problems, many of the more general results from rigorous analyses of random walks in random environments (Zeitouni 2004, 2006) do not apply.

Models

Let the original lattice from which the labyrinth is made have coordination number z . Then at a site s of the labyrinth, the coordination number will be $Z_\omega(s) \leq z$, where $Z_\omega(s)$ is determined by the specific realization ω of site or bond percolation used in constructing the labyrinth. There are two canonical choices for the ant’s mode of stepping through the labyrinth, the distinction between

them having been clearly drawn by Mitescu and Rousseny (1983) and Majid et al. (1984).

myopic ant (Pólya case) – On arrival at site $\mathbf{s}$, the ant looks at the $Z_\omega(\mathbf{s})$ adjacent sites onto which it is permitted to step, assigns each of them probability $1/Z_\omega(\mathbf{s})$, and chooses one of them at random.

blind ant – On arrival at site $\mathbf{s}$, the ant attempts to move to one of the z adjacent sites on the original lattice. If this move is not allowed for the labyrinth, the ant remains at site $\mathbf{s}$.

In a given time interval, a blind ant visits fewer distinct sites than a myopic ant.

It is generally believed that the qualitative properties of myopic (Pólya) ants and blind ants are similar, but there is an important difference when the ant is introduced on a finite cluster (Mitescu and Rousseny 1983): the “equilibrium” probability distributions of the ant, approached asymptotically as the number of steps grows without bound, differ for the two models. The existence of equilibrium probability distributions on finite clusters can be discussed from the point of view of Markov chains (Feller 1970; Kemeny and Snell 1976), where such distributions are called “invariant measures” or “stationary distributions.”

Some early simulation results are shown in Fig. 3. These and subsequent simulations suggest (Duering and Roman 1991; Mitescu et al. 1978; Pandey et al. 1984; Seifert and Suessenbach 1984) that when the mean-square displacement $\langle R_n^2 \rangle$ is averaged over environments, as $n \rightarrow \infty$ we have

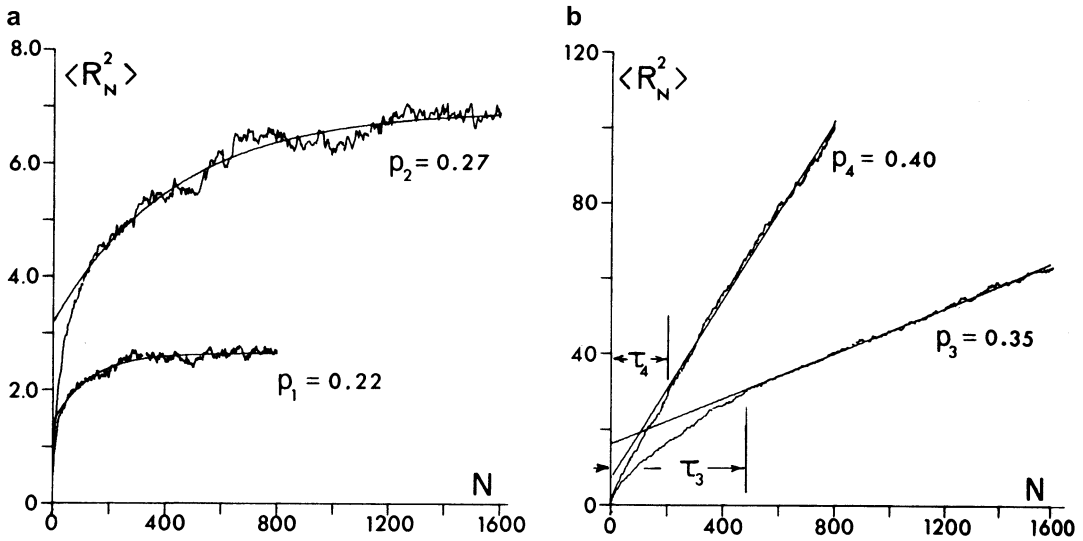
$$\overline{\langle R_n^2(p) \rangle} = \begin{cases} R_\infty^2 - A(p) \exp \{ [-n/\theta(p)]^w \} + \dots, & p < p_c, \\ Bn^{2k} + \dots, & p = p_c, \\ cD(p)n + \dots, & p > p_c, \end{cases} \quad (90)$$

where any dependence of a quantity on p or n is explicitly indicated. Here $D(p)$ is an effective diffusion constant, c is a lattice-dependent constant, and the exponent k , which would be $1/2$ for classical diffusion, is dimension-dependent, with $k < 1/2$ in low-dimensional systems. In particular, estimates of k for the simple cubic lattice are

0.20 ± 0.01 (Pandey et al. 1984) and 0.200 ± 0.002 (Duering and Roman 1991). The value of the exponent w was initially believed close to 1 (Mitescu et al. 1978) in three dimensions, but later evidence (Pandey et al. 1984) suggests that $w \approx 0.4$ in three dimensions.

The time-evolution of the position of the ant in the labyrinth for $p \leq p_c$ gives an excellent illustration of the distinction between quenched results (results that hold in a specific realization of percolation on the lattice) and annealed results (results averaged over all realizations of percolation on the lattice). For $p \leq p_c$ the ant commences with probability 1 on a cluster of finite size, and in any individual realization ω of the system, the mean-square displacement will converge to a finite value (blind case) or oscillate between two finite values (myopic case for some lattices, where oscillations can occur if the cluster divides into sites accessible only after an even number of steps and sites accessible only after an odd number of steps). For $p = p_c$, at a given value of n the displacement will have saturated (i.e., be close to its asymptotic value) in some environments but not in others. This partitioning of the realizations of the environments, and the tortuous structure of large clusters that are not yet fully explored by the ant, gives rise to the nonclassical exponent $k < 1/2$.

Above the percolation threshold, since diffusive behavior is anticipated, and the steady-state diffusion problem is equivalent to an electrical conduction problem, $D(p)$ should vanish as $p \downarrow p_c$ with the same critical exponent t as the effective conductivity. The earliest ant-in-the-labyrinth simulations above the percolation threshold (Mitescu et al. 1978) produced lower estimates of the conductivity exponent t than those obtained by other methods. Nearly two decades later, Poole and Salt (1996) simulated blind ant walks of up to 10^6 steps in square lattice site percolation for $p > p_c$, and found evidence that $\langle R_n^2 \rangle^{1/2} = D(p)n^{1/2} + C(p) + \dots$, reflecting a very slow relaxation towards diffusive asymptotic behavior, rather than a well-defined crossover between fractal and diffusive regimes. They report that $D(p) \propto (p - p_c)^t$ as $p \downarrow p_c$ with $t = 1.291 \pm 0.024$, consistent with the most credible alternative estimates of t (Table 2).



Conduction and Diffusion in Percolating Systems, Fig. 3 Simulations of the ant in the labyrinth (Mitescu et al. 1978): myopic ants (Pólya walkers) on the simple cubic lattice under site percolation ($p_c \approx 0.31$) for four values of p . Simulation data (erratic curves) shows the mean-square displacement after N steps, averaged over realizations of the environment when a fraction p of all sites are occupied: (a) shows two cases with $p < p_c$ ($p_1 = 0.22, p_2 = 0.27$), with the smooth curves least-squares fits to $R_\infty^2 -$

$A(p) \exp[-n/\theta(p)]$; (b) shows two cases with $p > p_c$ ($p_1 = 0.35, p_4 = 0.40$), with the straight-line asymptotes corresponding to effectively diffusive behavior and τ_k corresponding to the number of steps needed for diffusive behavior to be manifest for $p = p_k$. For a more careful discussion of the approach to diffusive behavior as $N \rightarrow \infty$ for $p > p_c$, based on simulation of much longer walks, see Poole and Salt (1996). (Figure reproduced with permission from Mitescu et al. (1978))

Scaling Theory for the Ant in the Labyrinth

Heuristic work (Ben-Avraham and Havlin 2000; Havlin et al. 1983; Hughes 1996; Pandey and Stauffer 1983; Stauffer and Aharony 1994) raises attractive possible connections between exponents characterizing the asymptotic behavior of the ant in the labyrinth and the geometrical exponents of percolation theory. A number of rigorous scaling relations involving various exponents that characterize random walk and electrical conduction on lattices have been derived by Telcs (2006), but these are not sufficiently informative to establish rigorously the results now briefly described or to enable exponent values to be predicted.

We shall denote averages for walks, conditioned on the walks taking place on clusters of m sites, by $\langle \cdot \rangle_m$. Consider first the expected number of distinct sites visited. At the percolation threshold, if there is some kind of effective harmonic dimension for large clusters (cf. section “Lattice Problems”), which one might loosely call the harmonic dimension of the incipient

cluster (cf. section “The Incipient Infinite Cluster”) and denote by H_{ic} , then the expected number of distinct sites visited by a walker on a cluster of m sites should evolve as $\langle S_n \rangle_m \propto n^{H_{\text{ic}}/2}$ for $1 \ll \langle S_n \rangle_m \ll m$. The scaling hypothesis (Pandey and Stauffer 1983) $\langle S_n \rangle_m \approx n^{H_{\text{ic}}/2} \phi(m/n^{H_{\text{ic}}/2})$ and the asymptotic law $P_m(p) \propto m^{-1-1/\delta}$ for the cluster size distribution gives a simple prediction (Angles d’Auriac and Rammal 1983; Pandey and Stauffer 1983) for the mean number of distinct sites visited, averaged both over cluster sizes and over walks on individual clusters:

$$\begin{aligned} \langle \overline{S_n} \rangle &\approx \sum_{m=1}^{\infty} m^{-1-1/\delta} n^{H_{\text{ic}}/2} \phi\left(m/n^{H_{\text{ic}}/2}\right) \\ &\approx n^{(-1-1/\delta)H_{\text{ic}}/2}; \end{aligned} \quad (91)$$

the last result arises from approximating the sum by an integral. Three-dimensional simulations give $\langle \overline{S_n} \rangle \propto n^{0.54 \pm 0.02}$ (Pandey and Stauffer 1983).

A similar analysis may be performed for the mean-square displacement at the percolation threshold (Gefen et al. 1983; Hughes 1996). If the fractal dimension of the incipient infinite cluster is denoted by d_{ic} (cf. section “[The Incipient Infinite Cluster](#)”), one may propose that the mean-square displacement on clusters of size m is $\langle R_n^2 \rangle_m \propto n^{2v_{\text{ic}}}$ for $1 \ll \langle R_n^2 \rangle_m^{1/2} \ll m^{1/d_{\text{ic}}}$. The naturally associated scaling assumption $\langle R_n^2 \rangle_m \approx n^{2v_{\text{ic}}} \psi(m^{1/d_{\text{ic}}} / n^{2v_{\text{ic}}})$ predicts the mean-square displacement averaged both over cluster sizes and over walks on individual clusters to be

$$\begin{aligned} \overline{\langle R_n^2 \rangle} &\approx \sum_{m=1}^{\infty} m^{-1-1/\delta} n^{2v_{\text{ic}}} \psi\left(m^{1/d_{\text{ic}}} / n^{2v_{\text{ic}}}\right) \\ &\approx n^{2v_{\text{ic}}[1-d_{\text{ic}}/(2\delta)]}. \end{aligned} \quad (92)$$

The accepted scaling relations $d_{\text{ic}} = (\beta + \gamma)/v$ and $\gamma = \beta(\delta - 1)$ give the alternative form $\overline{\langle R_n^2 \rangle} \propto n^{2v_{\text{ic}}[1-\beta/(2v)]}$ and simulation data is consistent with this picture (Havlin and Ben-Avraham 1983).

A number of other observable quantities can be estimated by scaling arguments (Ben-Avraham and Havlin 2000; Hughes 1996; Stauffer and Aharony 1994). For example, just below the percolation threshold, it is predicted (Stauffer 1985) that the mean-square displacement (averaged over all walks and realizations) has the limiting value $R_{\infty}^2 \propto (p_c - p)^{2v-\beta}$.

The Alexander-Orbach Conjecture

The publication in 1982 of a conjecture of Alexander and Orbach (1982) that $H_{\text{ic}} = 4/3$ for all dimensions d briefly raised the possibility that the conductivity exponent t could be simply related to geometrical exponents in percolation theory, and that other dynamical exponents related to random walk processes could be determined. Given the accepted exact values for geometrical exponents in two dimensions, the Alexander–Orbach conjecture predicted that $t = 91/72 \approx 1.2639$ in two dimensions. This prediction is clearly inconsistent with the best estimates of t given in Table 2 and it has become generally accepted that the Alexander–Orbach conjecture, while an excellent approximation for two or three-dimensional

lattices, is not precisely correct (Ben-Avraham and Havlin 2000; Nakayama et al. 1994).

In 2009, Kozma and Nachmias (2009) proved rigorously that a precisely formulated version of the informally stated Alexander–Orbach conjecture is true for ordinary site percolation on the d -dimensional hypercubic lattice $\mathbb{Z}^d$ if $d \geq 19$ and for a spread-out lattice percolation model for $d > 6$. It is likely that their theorem is true for $d > 6$ for site percolation on $\mathbb{Z}^d$ and all other reasonable periodic lattices, but this remains to be established. Analogues of the results of Kozma and Nachmias have been proved for trees (Barlow and Kumagai 2006; Kesten 1986b) and for directed percolation (Barlow et al. 2008).

In the theorem stated below, the probability measure for the incipient infinite cluster in terms of which the statement “with probability 1” is made is defined as follows: at $p = p_c$, probability conditional on the event that the walk origin $\mathbf{s}_0$ and a site with position vector $\mathbf{s}_0 + \mathbf{l}$ are part of the same cluster of occupied sites in standard site percolation, and let $|\mathbf{l}| \rightarrow \infty$. (This is a variant of one of Kesten’s two equivalent definitions of the incipient infinite cluster, which would otherwise be a nebulous concept: see section “[The Incipient Infinite Cluster](#)”)

Theorem of Kozma and Nachmias. Let $p_n(\mathbf{s}_0)$ denote the probability that a (myopic) ant is found at the starting site on the n th step, let T_r denote the first passage time to a distance r from the starting site, and let S_n denote the number of distinct sites visited in the first n steps. Let angle brackets denote averaging over the randomness of the walk in a fixed realization of the incipient infinite cluster. Then for $\mathbb{Z}^d$ with $d \geq 19$, with probability 1 for the incipient infinite cluster,

$$\begin{aligned} \lim_{n \rightarrow \infty} \frac{\log p_{2n}(\mathbf{s}_0)}{\log n} &= -\frac{2}{3}, \quad \lim_{r \rightarrow \infty} \frac{\log \langle T_r \rangle}{\log r} = 3, \\ \lim_{n \rightarrow \infty} \frac{\log \langle S_n \rangle}{\log n} &= \frac{2}{3}. \end{aligned}$$

The first and third results can be interpreted as the system having harmonic or spectral dimension $4/3$, cf. section “[Nearest-Neighbor Stepping Discrete-Time Random Walk](#).” For related results, see also Kumagai and Misumi (2008) and Heydenreich et al. (2014).

Rigorous Results for Discrete Time

The most important rigorous result is probably the following theorem, which shows that Pólya's simple criterion for transience $d \geq 3$ is not destroyed by the percolation process, provided the system is above the percolation threshold, and the ant starts on the infinite cluster (Grimmett et al. 1993).

Theorem of Grimmett, Kesten, and Zhang. For myopic ants (Pólya walkers) walking on the infinite cluster generated by bond percolation on the simple hypercubic lattice at $p > p_c$, the walk is transient with probability 1 if $d \geq 3$.

As with most rigorous results in this area, the proof is of antisocial length. However, Rayleigh's Monotonicity Law and the correspondence between random walks and electric circuits makes it relatively straightforward to show that the recurrence of the ordinary Pólya walk on the square lattice $\mathbb{Z}^2$ ensures the recurrence of myopic ant motion on every realization of an infinite cluster in bond or site percolation on the square lattice.

For walks on the incipient infinite cluster, made precise by either of the equivalent approaches of Kesten discussed in section "The Incipient Infinite Cluster," it is known (Kesten 1986c) that the general behavior is subdiffusive ($|\mathbf{X}_n| = O(n^{1/2 - \epsilon})$ for some $\epsilon > 0$) for the square lattice bond problem, but the exact exponent characterizing the growth of $|\mathbf{X}_n|$ is unknown.

Rigorous Results for Continuous Time

For the natural master-equation analogue of the myopic ant (corresponding to a myopic ant executing a continuous-time random walk with an exponential waiting time density of mean waiting time 1 at all sites), several exact results that mirror known results for Pólya walks on periodic lattices are available. In stating these results, we assume that our labyrinth is generated by bond percolation on $\mathbb{Z}^d$ with $d \geq 2$ and $p > p_c$, we write C_∞^ω to denote the (unique with probability 1) infinite cluster in the realization ω of the random environment, and we assign coordinates such that the origin $\mathbf{0}$ is a site of the infinite cluster. We write Pr^ω to denote probabilities associated with random walks in the fixed realization ω of the environment. The position at time t of a random

walker starting from the origin at time 0 is $\mathbf{X}_t$. We say that a result holds for almost all environments if it holds with probability 1, where probability is measured with respect to the realizations of bond percolation for the given value of p .

The following results, published in 2004 (Barlow 2004; Mathieu and Remy 2004), go further than results previously established only for $d = 2$ (de Masi et al. 1985, 1989) and show that there is no anomalous behavior above the percolation threshold for the myopic ant problem for all $d \geq 2$: in the long time limit, the process strongly resembles classical diffusion.

Mathieu and Remy (2004) have proved that there exists $c_1(p, d)$ (independent of time or the realization ω of the environment) such that for almost all environments, the quenched bound

$$\sup_{\mathbf{y} \in C_\infty^\omega} \text{Pr}^\omega \{ \mathbf{X}_t = \mathbf{y} \} \leq \frac{c_1(p, d)}{t^{d/2}} \quad (93)$$

holds. This result confirms the transience of the walk for $d \geq 2$, a result already known from the theorem of Grimmett, Kesten, and Zhang (1993) for the discrete-time walk, stated in section "Rigorous Results for Discrete Time." Mathieu and Remy also establish the analogous result to (93) for site percolation on the two-dimensional square lattice, and an annealed lower bound proportional to $t^{-d/2}$ for bond percolation on $\mathbb{Z}^d$.

Barlow (2004) has constructed upper and lower bounds for the quenched transition density

$$q_t^\omega(\mathbf{x}, \mathbf{y}) = \frac{1}{Z^\omega(\mathbf{y})} \text{Pr}^\omega \{ \mathbf{X}_{t+\tau} = \mathbf{y} | \mathbf{X}_\tau = \mathbf{x} \} \quad (94)$$

that hold with probability 1 for sufficiently large time t :

$$\begin{aligned} & \frac{c_1(d, p)}{t^{d/2}} \exp \left[-\frac{c_2(d, p)}{t} |\mathbf{x} - \mathbf{y}|_1^2 \right] \\ & \leq q_t^\omega(\mathbf{x}, \mathbf{y}) \\ & \leq \frac{c_3(d, p)}{t^{d/2}} \exp \left[-\frac{c_4(d, p)}{t} |\mathbf{x} - \mathbf{y}|_1^2 \right]. \end{aligned} \quad (95)$$

Here if $\mathbf{x} = (x_1, x_2, \dots, x_d)$ and $\mathbf{y} = (y_1, y_2, \dots, y_d)$, one defines

$$|\mathbf{x} - \mathbf{y}|_1 = \sum_{k=1}^d |x_k - y_k|. \quad (96)$$

Sufficiently large t is quantified by $t \geq \sup\{|\mathbf{x} - \mathbf{y}|_1, S_{\mathbf{x}}^{\omega}\}$, where the finite but realization-dependent quantities $S_{\mathbf{x}}^{\omega}$ deal with problems associated with an initial period of potentially anomalous behavior. Barlow's results establish the essentially diffusive asymptotic behavior of the walk. For further results in the quenched case, including convergence of a suitably scaled displacement to Brownian motion in almost all realizations of the random environment, see Berger and Biskup (2007), Mathieu and Piatnitski (2007), and Sidoravicius and Sznitman (2004).

The above results pertain only to walks of Pólya type on the infinite cluster for $p > p_c$. For a discussion of biased random walks on the infinite cluster in two-dimensional percolation, see Berger et al. (2007). Hambly and Kumagai (2010) give some exact results for a particular recursively defined pseudolattice (the diamond hierarchical lattice) at $p = p_c$. Biskup (2011) has given a general review of the “random conductance model” of a random walk in a random environment, which includes as a special case the ant in the labyrinth for $p > p_c$.

Future Directions

Problems of transport and conduction in random systems subject to the kinds of uniform ellipticity restrictions that preclude percolation phenomena have become increasingly well understood. The address by Zeitouni (2002) at the 2002 International Congress of Mathematicians summarized a number of areas in which progress on the problem of random walk in a random environment remained to be made and there has been considerable progress. However, adequate theoretical understanding does not entirely remove the tedious problem of accurately estimating overall system properties.

The situation concerning truly percolative problems remains less satisfactory. The generally

classical behavior of such systems above the percolation threshold means that, for modeling purposes in science and technology, one often may reasonably replace the random system by a uniform analogue, in much the same way as one can do this for systems with ellipticity restrictions, but with the important caveat that close to the percolation threshold, the length, or timescales at which the uniform treatment is accurate may in practice be unacceptably large. A fuller understanding therefore of processes at or near the percolation threshold remains the greatest challenge.

There has been spectacular progress since the late 1970s with the understanding (both heuristic and rigorous) of the geometrical side of percolation theory, especially for lattices. We have elegant results on the existence of classical or mean-field behavior for large dimension d , and the knowledge (though gaps in rigor remain) that mean-field behavior applies for $d \geq 7$ and in a slightly weaker sense for $d = 6$ but not for smaller d . More importantly, through rigorous work on conformal invariance and on Schramm–Loewner evolution processes, exact two-dimensional values of geometrical critical exponents and exact two-dimensional scaling relations are now properly established. An analogous rigorous account of dynamical exponents characterizing transport in two-dimensional percolating systems is perhaps not too much to ask for, though the way is not yet clear. It would be surprising indeed if there were significant progress in the short term on the rigorous analysis of three-dimensional systems at or near the percolation threshold.

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Percolation in Porous Media

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Article Outline

Glossary

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Glossary

Anisotropy There is anisotropy when the global physical property of the system is direction dependent.

Breakthrough time The time for convection of a single phase passive tracer between an injection well and a production well.

Capillary dominated flow A flow regime in which the only dominant driving force is due to capillarity.

Connectivity The fraction of occupied sites belonging to the percolating clusters i.e. represents the strength of the percolating cluster.

Continuum percolation Percolation on continuum spaces with randomly distributed geometrical objects where there is no lattice at all.

Field scale This represents large scale heterogeneities at reservoir level or the kilometer scale.

Finite size scaling A scaling law within percolation theory which deals with the effects of the finite boundaries.

Fracture Any discontinuity within a rock mass which developed as a response to stress.

Invasion percolation Another kind of percolation theory appropriate for describing the structure and amounts of two immiscible fluids at breakthrough.

Modeling Describing physical phenomena under nature's law in some mathematical relations, e.g. governing fluid flow, to better understand the system and to predict its behavior.

Percolation threshold A particular value of occupancy probability at which one large cluster spans the whole region.

Permeability The "conductance" of the rock to fluid flow determined from Darcy's Law that the flow rate is proportion to the applied pressure gradient and inversely proportional to the fluid viscosity, the constant of proportionality is the permeability.

Pore scale This represents pore throat level or the micron scale.

Porous media A medium consists of rock grains and disordered void spaces of approximately 10–100 μm across usually occupied by oil, water and gas in a typical hydrocarbon reservoir and characterized by porosity and permeability.

Simulation Numerical model for solution to the mathematical equations which be able to predict the physical behavior of the system.

Uncertainty The estimated amount or percentage by which an observed or calculated value may differ from the true value.

Definition of the Subject

Porous media are important in many areas including hydrocarbon reservoir engineering, hydrology and environmental engineering. They are also important in, for example, fuel cells, many industrial process and biological systems (lungs, bones, capillary networks and termite nests are all biological examples). Understanding the structure of porous media and the physics of fluid flow in porous media is of great interest. For example, choosing the efficient recovery techniques by

reservoir engineers requires understanding of how different fluids and the porous media interact at different scales by simulating the fluid flow in the reservoir under variety of conditions. The exchange and transport of reagents in fuels cells governs their efficiency. Percolation theory which describes the connectivity of a system mathematically (Broadbent and Hammersley 1957; Stauffer and Aharony 1992) has also many important applications from the spread of diseases and forest fires to the connectivity of geological entities (e.g., sandbodies or fractures) in porous media used for nuclear waste disposal or for hydrocarbon recovery (Sahimi 1994). Percolation concepts have been used to model fluid movement in porous media and fractured rocks at both pore scale (mm) and reservoir scale (km). At the pore scale a network of pore and throats is used to study the immiscible displacement and estimate the capillary pressure and relative permeabilities. At the field scale, the permeability map is split into either permeable (flow units e.g. good oil bearing sands) or impermeable (background e.g. shale) and assumes that the connectivity of flow units controls the flow movement. Then percolation theory is directly used to estimate static behavior (connectivity – i.e. connected fraction of good oil bearing sands) and dynamic behavior (i.e. effective permeability across the reservoir, breakthrough time between an injector and a producer or post breakthrough behavior). In particular, the percolation approach is able to estimate the uncertainty in the reservoir performance parameters which is not possible with a single detailed conventional simulation model.

Introduction

Percolation theory is a mathematical model of the connectivity and conductivity in geometrically complex systems (Stauffer and Aharony 1992) first developed by Broadbent and Hammersley in Broadbent and Hammersley (1957). The full description of this theory and its applications to different disciplines can be found elsewhere (Berkowitz and Balberg 1993; Sahimi 1994; Stauffer and Aharony 1992). It links the global

geometrical and physical properties of the system to the number density of geometrical objects (representing geological entities, e.g., fractures) placed randomly in space through algebraic universal laws. By universality we mean the large scale behavior of the system is independent of the small scale details of the system, i.e. local geometries.

On the simplest example is an infinite lattice of sites which are occupied with a probability p . Clusters are formed as the neighboring sites are occupied and they are identified by using standard algorithm (Hoshen and Kopelman 1976). The clusters grow in size as the occupancy probability increases. Then, at particular value of p , called the percolation threshold p_c^∞ , one large cluster spans the whole region. There are also other small clusters which get absorbed as p further increases. For the infinite lattice there are some simple power law or scaling laws which describe the behavior of the system around the threshold p_c^∞ such as $P(p) \propto (p - p_c^\infty)^\beta$ and $\xi(p) \propto |p - p_c^\infty|^{-\nu}$ where $P(p)$ is the probability that an occupied site belongs to the spanning cluster (so called connected fraction or connectivity) and $\xi(p)$ is the correlation length (which is a measure of the “typical” size of the clusters, excluding the infinite cluster when above the threshold). Note that the correlation length ξ is related to the two point correlation function $g(r)$, which is the probability that two sites separated by a distance r are in the same cluster. The critical exponents β and ν are independent of the kind of the lattice or even if there is a lattice or not (continuum system) they only depends on the dimensionality of space (i.e. 2D or 3D). Values for $\beta = 5/36$ and 0.4 (in 2 and 3 dimensions respectively), and $\nu = 4/3$ and 0.88 (Stauffer and Aharony 1992). This is known as *universality* and is an important concept in percolation theory which enables us to study and understand the behavior of a very wide range of systems without needing to worry too much about the small scale detail. However, the percolation threshold does depend on the detail of the lattice.

This is the basic framework of percolation theory. To be useful in the context of reservoir modeling we need to address some issues. Everything so far has been defined for an

infinite lattice. What happens if there is no lattice at all (i.e. continuum systems with randomly distributed geometrical objects) and when the system is finite. There is also the issue of how to modify these percolation laws for anisotropic systems, variable size and orientation distribution of objects and spatial correlation between objects.

Porous Media

The flows of fluids in porous media are related to many important industrial and geological applications, such as hydrocarbon recovery or ground water flow modeling (Dullien 1992; Sahimi 2011). The porous media are typically made from rock grains and disordered void spaces and are usually characterized by porosity ϕ (i.e. the storage capacity of a rock, in other words the volume fraction which is void or pore space) and permeability k (i.e. the “conductance” of the rock to fluid flow determined from Darcy’s law that the flow rate is proportion to the applied pressure gradient and inversely proportional to the fluid viscosity, the constant of proportionality is the permeability). The pore spaces are approximately 10–100 μm across and are usually occupied by oil, water and gas (in a typical hydrocarbon reservoir). However, the reservoir itself may be several kilometers in extent. Fluid displacement in porous media depends on the scale and can be controlled by several forces including capillary forces (mostly at the pore scale), viscous forces and gravity forces. Hence, the type of displacement observed depends on the capillary number, which is the ratio of the viscous pressure drop at the pore scale to the capillary pressure, and the Bond number, which is the ratio of the hydrostatic pressure drop over a pore to the capillary pressure. It should be noticed that the full description of displacement process in porous media is very difficult due to the variety of physical phenomena. For example, the flow of two immiscible fluids depends on the wetting properties of the two fluids, their viscosity ratio, their respective densities, and the displacement rate. Typical flow rates in reservoirs are of order of a few feet (10’s of

centimeters) a day. Hence, on the pore level the flow is controlled almost entirely by capillary forces between immiscible oil and water. However, over large distances viscous and buoyancy forces dominate (Wilkinson 1984). To study the efficient recovery techniques (e.g. water flooding), it is necessary to simulate the fluid flow at the reservoir scale. Even with the today’s modern computers, the simulation cannot be achieved at the pore scale (typically there would be of the order of 10^{21} pores in a reservoir). The conventional approach is to establish the simulation on a grid of roughly 100 m linear size which represents displacements occurring within millions of pores. The small scale physics is then represented by parameters in macroscopic partial differential equations to describe the transport of fluid in the field scale simulation. These parameters can be measured experimentally on representative core samples or they can be estimated from pore and throat network models (e.g. percolation based models).

The basic equation at the continuum scale is Darcy’s law, which states that the flow rate is proportional to the applied pressure gradient and inversely proportional to the fluid viscosity

$$\mathbf{v} = -\frac{K}{\eta} \nabla P \quad (1)$$

where K is the rock permeability. Some analysis shows that it has dimensions of area and for typical reservoir rocks it is of the order of 10^{-12} m^2 , which is about the cross sectional area of a typical pore throat (although more detailed calculations are required to obtain better estimates than this). The permeability can vary by orders of magnitude over very short differences reflecting the heterogeneity in pore size arising from the complex processes of geological deposition. This law is used in conjunction with the assumed incompressibility of the fluid to give an equation for the fluid pressure.

$$\nabla \cdot \mathbf{v} = \nabla \cdot K \nabla P = 0. \quad (2)$$

When there are two or more fluid phases present this basic law gets modified to,

$$v_i = - \frac{Kk_i(S_i)}{\eta_i} \nabla P_i \quad (3)$$

where k_i is the relative permeability of phase I , which is usually assumed to be a function of the fluid saturations S_i only, but it depends, in principle, on other factors as well. Fluid saturation is the fraction of the volume of the pore space occupied by the phase. Along with the incompressibility condition for the total flux we also have a conservation law for each phase as,

$$\phi \frac{\partial S_i}{\partial t} + v_i \cdot \nabla S_i = 0 \quad (4)$$

where ϕ is the porosity. This set of equations is the most basic set of equations used to describe multiphase flow in porous media. Typically the parameters (such as porosity, permeability and relative permeabilities) are determined empirically. There is really no microscopic averaging of the pore scale physics to determine these, although recent studies using percolation as one approach are an attempt to do this (as described in the next section). In reality more complex equations incorporating further physics (such as the phase behavior) are often included also.

The pore scale porous media can be simply modeled as a network of bonds, i.e., pore throats and sites, i.e., pore bodies to study the flow behavior. Then a series of displacement steps in each pore or throat are combined to simulate the flow movement. The idea was first used by Fatt (1956) and since then, the capabilities of network and percolation based models have improved enormously (Blunt and King 1990; Blunt et al. 1992; Chandler et al. 1982; Dijkstra et al. 1999; Fenwick and Blunt 1998; Knackstedt et al. 2001; Koplik and Lasseter 1985; Mohanty and Salter 1982; Øren et al. 1998; Pereira et al. 1996; Piri and Blunt 2002; Valvatne and Blunt 2003; Wilkinson and Willemsen 1983). Invasion percolation is a typical example for modeling capillary dominated regime of flow in porous media (Wilkinson and Willemsen 1983) and will be more fully described in the next section. The models are then used to find capillary pressure and/or relative permeability (Blunt and King 1990; Diaz et al. 1987; Heiba

et al. 1992; Mani and Mohanty 1998; Maximenko and Kadet 2000; Soll and Celia 1993). For example, Soll and Celia (1993) developed a pore scale capillary-dominated flow model by neglecting the viscous forces but considering the gravity effect (which modifies the local capillary pressures) to simulate capillary pressure-saturation relationships in a water-wet system. Moreover, Paterson et al. (1997) used a percolation model with trapping to study the effects of spatial correlations in the pore size distributions on the relative permeabilities and residual saturations. They found lower residual saturations for correlated properties in comparison to uncorrelated ones.

At the field scale, heterogeneities which affect the flow behavior appear on all length scales from microns to tens of kilometers and have to be modeled to make reliable predictions of future reservoir performance. However, there exist very few direct measurements of the flow properties. Core plugs directly measure the permeability but they represent a volume of roughly 10^{-13} of a typical reservoir. Well logs and well tests measure large volumes (10^{-4} and 10^{-7} respectively) but the results have to be interpreted to infer flow properties. The flow itself takes place on the scale of the pores which are typically around 10^{-21} of the volume of the reservoir. The consequence is a great deal of uncertainty about the spatial distribution of the heterogeneities which influence the flow. The conventional approach to this is to build detailed reservoir models (note that the largest of these has around 10^7 grid blocks, so they fall very short of the actual level of heterogeneity that we know about), upscale or coarse grain them to around 10^4 or 10^5 grid blocks and then run flow simulations. These models need to be taken from a whole range of possible models with a suitable probability attached to each to determine the uncertainty in performance. The problem with this approach is that it is computationally very expensive. Therefore, there is a great incentive to produce much simpler models which can predict the uncertainty in performance much quicker. These models must be based on the dominant physics that control the displacement process. The percolation approach based on the connectivity of flow units is one very quick

method to model flow and predicts uncertainty in the reservoir performance parameters. This will be further described in section “[Application of Percolation to the Field Scale](#)”.

Application of Percolation to Pore Scale

Let’s start with a simple case of displacement of a fluid by second fluid in a two-phase system, i.e., the problem of oil/water flooding. Fluid movement can be governed by viscous, gravity and capillary forces (Bear 1972). For systems without gravity we expect different flow regimes depending on the capillary number. Viscous forces in the two fluids may be different mainly because the viscosity of the fluids is different. The high viscosity of the displaced fluid can leads to a highly unstable displacement pattern with a rapid breakthrough of the non-wetting fluid into the wetting fluid called viscous fingering (Chen and Wilkinson 1985; Homsy 1987). We neglect this by considering the situation that the displacing fluid has a viscosity higher than or equal to the viscosity of the displaced fluid. Then, for slow displacements the invasion percolation can be used to describe the structure and amounts of fluids in a two-phase displacement at breakthrough when the invading fluid is completely nonwetting (Chandler et al. 1982; Lenormand and Bories 1980; Wilkinson and Willemsen 1983). The displacement in the network (or model) is based on physical principles (i.e. the heterogeneity of the capillary pressures along the interface). Consider a lattice with sites and bonds representing pores and throats respectively (with the pores as spheres and the throats as cylinders in three dimensions). The throats can be classified into allowed (those can in principle be invaded by that phase ignoring the effect of surrounding bonds), occupied (those that are occupied by that phase) and accessible (those that are allowed by the phase but also the surrounding bonds will not inhibit the fluid to try). Two processes can be considered for an immiscible displacement. An event where a wetting phase (i.e. water) is displaced by a non-wetting phase with a positive capillary pressure is called drainage. The process where the wetting phase (i.e. water) enters the

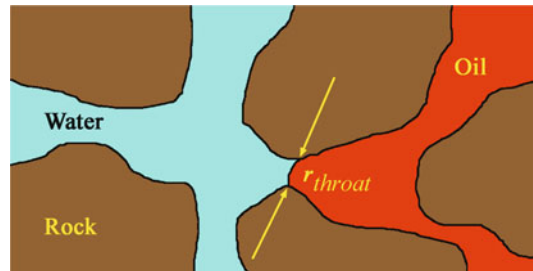
porous medium and displaces the non-wetting phase is called imbibition. In practice, the capillary pressure for imbibition is lower than that for drainage.

Here, we describe how invasion percolation works for drainage. This is the simplest situation and the extension to other process can be found in the literature. First, consider a simple pore with a single interface between the fluids (Fig. 1). In order to overcome the pressure caused by the interfacial pressure to drive the non-wetting phase (oil) into the wetting phase (water) occupied pore, we need to apply a pressure of

$$P_c = \frac{\gamma \cos \theta}{r_{\text{throat}}} \quad (5)$$

where γ is the interfacial tension, θ is the contact angle and r_{throat} is the pore throat radius. We now imagine a network of pores linked by throats of varying radii. As we increase the pressure applied to the invading non-wetting phase, it can be seen that the pores will fill from the largest first (as there the chapter pressure to fill is lowest). However, the pores can be filled only if they are connected to the inlet face of in contact with the non-wetting phase. Hence, in the simple network below (Fig. 2) the pores will fill in the order 1, 2, 3 and so on where the labels are in order of the throat radius (the invading fluid comes from the left). If this process is continued we get a not fully occupied structure (Fig. 3).

It can be seen that the displacement process is not very efficient and there are large regions unswept. This process has picked out the

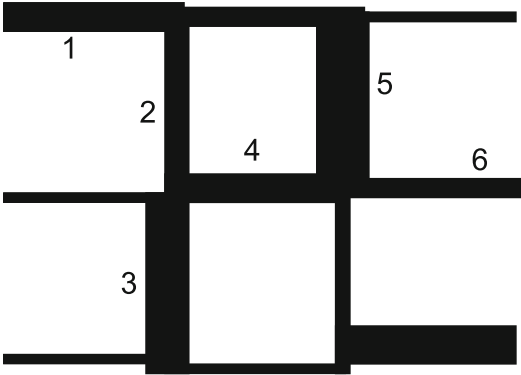


Percolation in Porous Media, Fig. 1 A schematic representation of a simple pore with a single interface between the non-wetting phase (oil) and the wetting phase (water)

percolation cluster of the network. If the bonds are ordered and a threshold applied such that (starting with largest first) a fraction of bonds equal to the percolation threshold are occupied, a pattern such as this will be found, except that none of the clusters not connected to the infinite cluster are found. This represents the fact that the invading fluid cannot “jump” from a current occupied site to some other interior site. Flow can only take

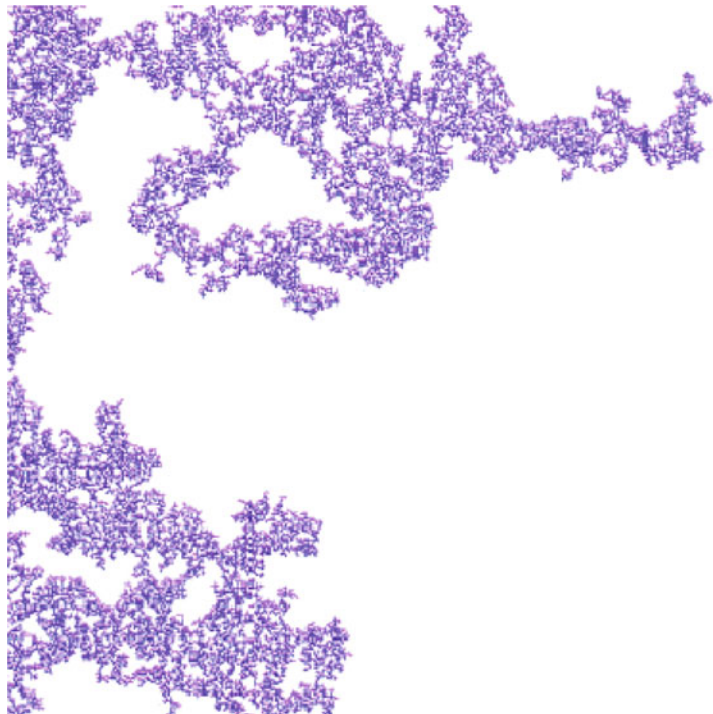
place through sites already connected to the inlet. This is the simple model of invasion percolation as introduced by Koplik and Lasseter (1985) and Wilkinson and Willemsen (1983).

The main quantities of interest are the fraction of sites which become occupied by the invader, and the distribution of random numbers of those sites. In invasion percolation with no trapping the clusters exhibit fractal character with fractal dimension (see Mandelbrot 1982 for fractals) $D = 1.89$ and 2.52 in 2D and 3D respectively which are similar to the results obtained from random percolation. The fraction of volume occupied by the invader is proportional to the grid size to the power -0.11 and -0.48 for 2D and 3D cases respectively which are again consistent with the universal values derived from random percolation results. Hence, invasion percolation has the same universality class as random percolation. Invasion percolation with trapping causes the phenomenon of residual oil. Fractal dimension of invader cluster is 1.82 in 2D which is less than $91/48$ of random percolation with no significant difference in 3D. The fraction of volume occupied by the invader is proportional to the grid size to



Percolation in Porous Media, Fig. 2 A simple illustrative network of pores linked by throats of varying radii. The numbers represent the filling order of pores

Percolation in Porous Media, Fig. 3 A typical percolation structure obtained from invasion percolation simulations for drainage



power -0.18 in 2D. If we pursue with the invasion process beyond the point of percolation, a second percolation threshold is reached when the defender consists of isolated clusters only and the process stops. Then the system has reached residual oil saturation. Properties of invasion percolation are believed to be consistent with that of random percolation. However, the spanning clusters are not precisely the same. Effects of gravity were characterized through dimensionless Bond number (Birovljev et al. 1991; Méheust et al. 2002). Percolation theory can then be used to improve our understanding of relative permeability and capillary pressure curves in porous media (e.g. Heiba et al. 1992).

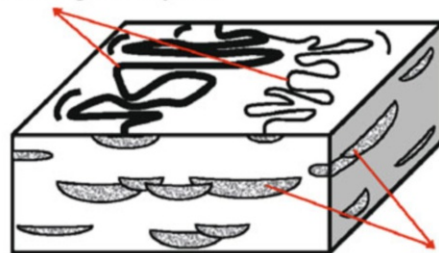
Whilst this process, is not what happens in the typical oil recovery process, it is a reasonable representation of the filling of an oil reservoir when the drops of oil formed in a source rock (typically some distance and much deeper than the final reservoir rock) moves under gravity and capillary forces to displace the water that originally in the reservoir rock.

Application of Percolation to the Field Scale

Here, we describe the application of percolation theory to, first, low to intermediate net-to-gross conventional reservoirs and secondly to fractured reservoirs. Consider, for example, a meandering river which deposits sand over time as represented schematically in Fig. 4. The deposited sand creates a sandbody which covers the meander belt. Occasionally, due to an event upstream, the river changes its path (called an evulsion by geologists) and deposits a new sandbody that may overlap with a previous body. The process continues and forms a system of embedded sandbodies in an impermeable background. Although there may be other depositional and post-depositional events, such as crevasse splays, mud drapes and shale layers which may alter this simple model, this simple model of overlapping sandbodies has been used (King 1990; Nurafza et al. 2006a, b) as the basic model for low to intermediate net-to-gross non fractured reservoirs.

Another example could be fracture networks. Field data obtained from large scale investigations

Meandering River System



Deposited Sandbodies

Percolation in Porous Media, Fig. 4 A meandering river system deposits sandbodies over the ages (Nurafza et al. 2006a)

show that the fracture network structure is close to the threshold and displays strong channeling patterns which can be explained by percolation theory (Cacas et al. 1990). It was found that in some natural fracture networks only a small percentage of fractures contributed to the permeability of the system (Sahimi 2011 and references therein). The large uncertainty associated with data and the lack of distinction between faults and joints makes it debatable whether or not natural fractures are well above the percolation threshold (highly interconnected) or near the threshold (poorly connected) (Berkowitz et al. 2000 and references therein). As pointed out by Berkowitz (2002), in some circumstances fracture networks seems to be highly connected, whereas in many other cases, where the fractures are created as a results of stress, the network is poorly connected which indicates that it is near the percolation threshold. These studies indicate that the application of percolation theory in many fracture networks is reasonable. Simple percolation models would assume that the fractures are randomly oriented and independently located in space; however, in reality fractures show different orientation distribution (Adler and Thovert 1999; Bear et al. 1993; Sahimi 2011; Zhang and Sanderson 2002) result from successive tectonic events and several length distributions such as power law (Heffer and Bervan 1990; Odling 1997; Segall and Pollard 1983; Van Dijk et al. 2000), log normal (e.g. Odling 1997; Rouleau and Gale 1985) or exponential (e.g. Priest and Hudson 1981; Rouleau and Gale 1985). There also exist spatial

correlation between fractures (Bonnet et al. 2001, and references therein) and cross correlation between fracture parameters such as correlation between aperture and the fracture size (e.g. Olson 2003; Vermilye and Scholz 1995) or cross correlation between the position of a fracture and its length (e.g. Bour and Davy 1999; Darcel et al. 2003a). We shall first discuss the very simple model of fractures (Balberg 1985; Balberg et al. 1983; Berkowitz 1995; Bour and Davy 1997, 1998; Charlaix 1986; Masihi et al. 2005; Robinson 1983) made by constant length randomly oriented and/or orthogonal fractures (Fig. 5).

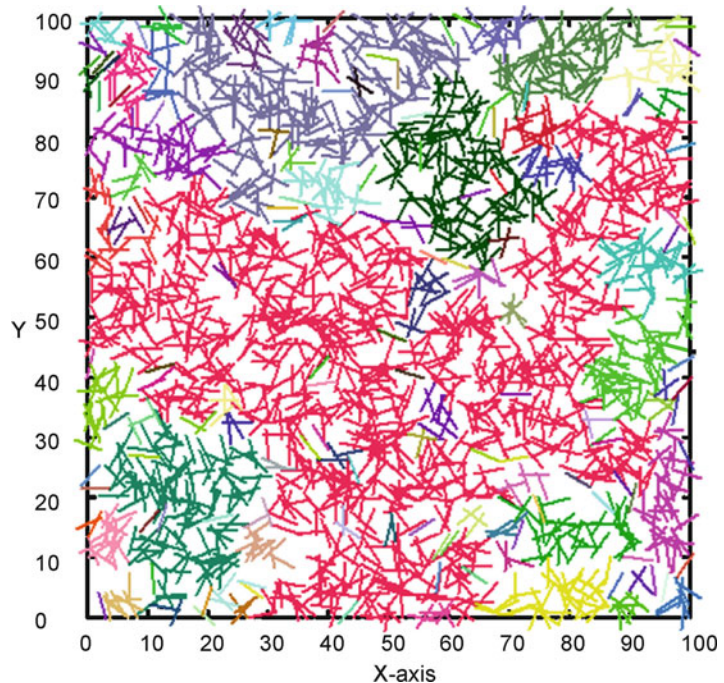
In these two examples, the objects (i.e. sandbodies and fractures) are not restricted to points on a fixed lattice so as there is no maximal concentration (notice that the upper bound of the occupancy probability in simple lattice percolation is one). In the case of fracture systems, for instance, there is theoretically no end to the degree of fracturing (Sahimi 2011) and fractures can be of any shape with variable length, direction and number of interconnected bonds (Berkowitz 1995). These lead us to use percolation on continuum spaces for these cases instead of using percolation on lattices.

Continuum Percolation

This is very straightforward because of the universality principle. We can place geometrical objects (e.g. rectangles representing sandbodies or line segments representing fractures in 2D space) randomly and independently (so called a *Poisson process*) in space. In place of the occupancy probability p we have the volume fraction of objects (or the probability that a point chosen at random lies within one of the objects) with the same notation, p . We get the same threshold phenomenon of a single cluster growing and dominating the system. The percolation threshold depends only on the shape of the objects, but for circles it is 0.678 ± 0.0024 and for squares it is 0.668 ± 0.0026 (similarly in 3D for spheres it is 0.288 ± 0.0016 and for cubes 0.276 ± 0.0013) so the difference is not very large and numerical experiments indicate that for reasonable convex (i.e. not very spiky) objects the threshold is around the same value. This is known as *continuum percolation*. Examples of applying percolation theory to uncorrelated (or even correlated) continuum systems that check the universality and determination of the percolation threshold of different models can be found elsewhere (e.g. Baker et al.

Percolation in Porous

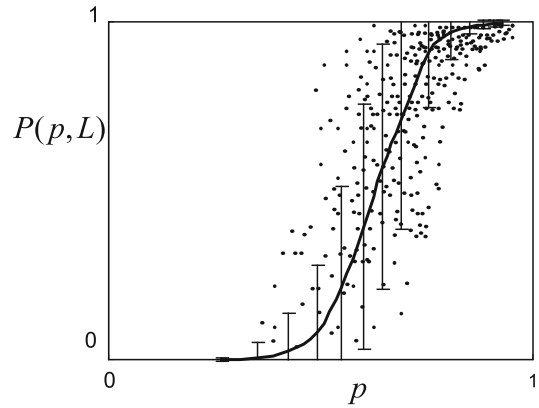
Media, Fig. 5 A randomly oriented fracture network ($l = 5$) at the threshold with 2066 fractures where the spanning cluster shown in red consists of 897 fractures



2002; Berkowitz 1995; Choi et al. 1995; Consiglio et al. 2004; Garboczi et al. 1995; Gawlinski and Stanley 1981; King 1990; Lee and Torquato 1990; Lin and Hu 1998; Lorenz and Ziff 2001; Xia and Thrope 1988). Extensive studies have shown that fracture systems, for example, belong to the general class of continuum percolation systems (e.g. Adler and Thovert 1999; Balberg et al. 1983; Berkowitz 1995; Koudine et al. 1998). From the principle of universality, the critical exponents are then fixed but the percolation threshold depends on the network topology. Previous estimations of critical exponents were successfully close to those from lattice percolation (e.g. Adler and Thovert 1999; Balberg et al. 1983; Bour and Davy 1997; Bour and Davy 1998; Charlaix 1986; Robinson 1984). Hence, from the principle of universality, we can use the same scaling laws with the same numerical values of the critical exponents as in lattice percolation. This is a remarkable result that we can now use.

Finite Size Scaling

The problem of how to deal with finite size systems is known as *finite size scaling*. The simple scaling laws described in section “[Introduction to Percolation Theory](#)” only apply to infinite-size systems. In a finite system, because of a sample-size, uncertainty there may be a connection at an occupancy very much less than the threshold value but still no connection at very high p values (greater than the threshold). This makes the definition of the percolation threshold of a finite system unclear, as a spanning cluster may appear in one realization and not in another at the same p . Therefore, for a finite system, an apparent threshold $\tilde{p}_c(L)$ which depends on the system size can be used. There have been several definitions of the apparent threshold in the literature (Adler and Thovert 1999; Berkowitz 1995; King 1990; Stauffer and Aharony 1992), such as the occupancy probability at which half of the realizations percolate. The percolation probability (i.e. connectivity) $P(p, L)$ can be defined as the fraction of occupied sites belonging to the spanning clusters. This is the finite size analogue of $P(p)$. If we plot $P(p, L)$ as a function of p over a large number of realizations for a particular



Percolation in Porous Media, Fig. 6 A typical scatter with the curve and the lines represent respectively the mean $P(p, L)$ and the standard deviation $\Delta(p, L)$ of connected fraction determined over all realizations at the same occupancy probability of a finite size system

system size (Fig. 6), we get a scatter of points from which we can determine the mean connected fraction $P(p, L)$ (the same notation as before) and the standard deviation $\Delta(p, L)$ (the fluctuations about this mean value).

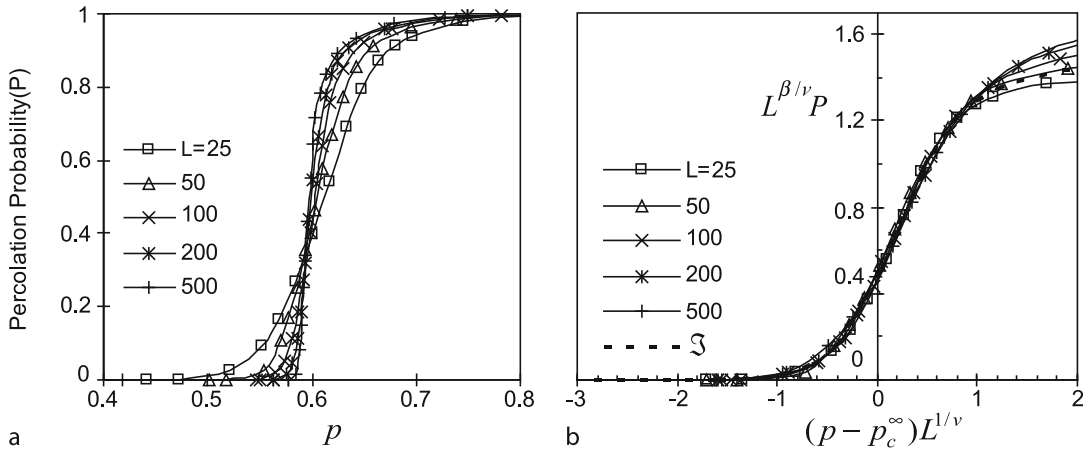
The effect of finite boundaries is to *smear out* the percolation transition (there is not a sharp transition in the connectivity as was exist in infinite systems). Plotting the mean connectivity $P(p, L)$ and the standard deviation of connectivity $\Delta(p, L)$ results obtained from different system sizes as a function of p gives different curves (Fig. 7a) which can be related to each other through the finite-size scaling law (Stauffer and Aharony 1992):

$$P(p, L) = L^{-\beta/\nu} \mathfrak{J} \left[(p - p_c^\infty) L^{1/\nu} \right] \quad (6)$$

$$\Delta(p, L) = L^{-\beta/\nu} \mathfrak{R} \left[(p - p_c^\infty) L^{1/\nu} \right] \quad (7)$$

where $\mathfrak{J}$ and $\mathfrak{R}$ are two scaling functions for the mean and standard deviation of connectivity, respectively. This means that, for example, if we plot $L^{\beta/\nu} P$ against $(p - p_c^\infty) L^{1/\nu}$ all the mean connectivity curves found previously should lie on top of each other to form a single universal curve $\mathfrak{J}$ (Fig. 7b).

It has been shown that all of the curves lie nearly on top of each other, except as



Percolation in Porous Media, Fig. 7 Plot of the mean connected fraction $P(p, L)$ showing: a the effects of finite boundaries on the percolation transition and b the data collapse using finite size scaling transformations

p approaches unity (Masihi et al. 2005; Nurafza et al. 2006a, b). This corresponds to the region where simple scaling breaks down. This region may be small in some cases and could be treated by using effective medium theory (Harris 1992; King 1990; Kirkpatrick 1973; Renshaw 1999; Snow 1969). It should be noticed that the scaling laws in Eqs. (6) and (7) are universal, but the scaling curves $\mathfrak{I}$ and $\mathfrak{R}$ depend on the model. These are very useful results, because once we get the two scaling curves from numerical simulations for a specific model, we can quickly predict the mean connectivity and its associated uncertainty for any other system sizes without performing any explicit realizations. Examples of the scaling master curves for the mean connectivity and the standard deviation of connectivity for fracture model and sandbodies model were given in Masihi et al. (2005, 2006a), and Nurafza et al. (2006a, b), respectively.

Anisotropy

The other problem that we have to deal with is due to anisotropy. By isotropy we mean that the horizontal connectivity is, on average, the same as the vertical connectivity if not for individual realizations. However, for many realistic systems, the objects or their orientation are rarely isotropic. For example, in fractured rocks fracture sets with particular orientations are typically formed as a result of tectonic history (Adler and Thovert 1999; Bear

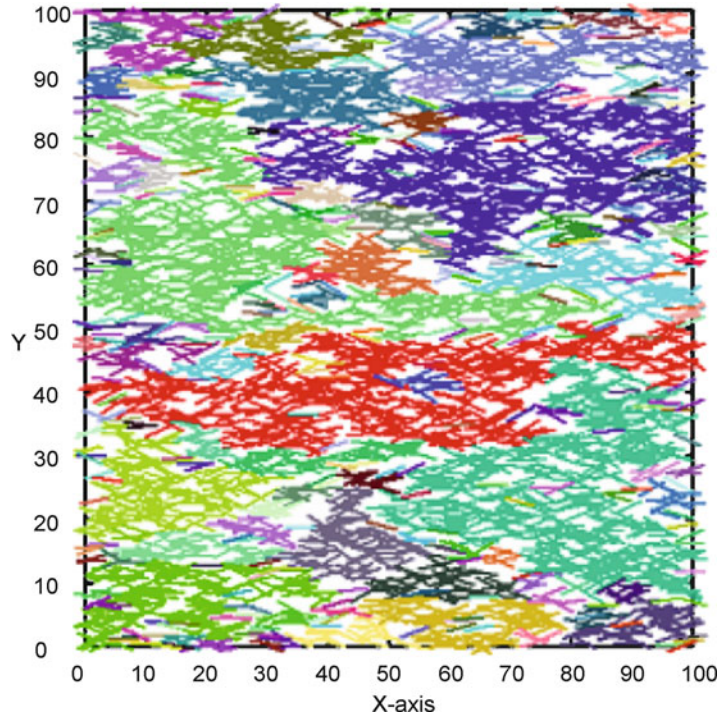
et al. 1993; Harris 1992; Sahimi 2011; Zhang and Sanderson 2002). This leads to the creation of an *easy* direction for connected paths which is in the short direction and a *difficult* direction which is along the long axis (Fig. 8).

The question is how to apply finite size scaling to anisotropic systems. This requires understanding the anisotropic behavior in percolation. A survey of the literature shows few studies on the subject among which are Monetti and Albano (1991) who performed Monte-Carlo simulations in an elongated geometry to obtain the dependency of the horizontal and vertical finite size percolation threshold to the aspect ratio of the lattice; Marrink and Knackstedt (1999) who assumed that an elongated lattice can be treated as a series of linked isotropic lattices; Hovi and Aharonyt (1996) who used renormalization group theory and duality arguments; Langlands et al. (1992) who found numerically the dependency of the crossing probability on the aspect ratio of rectangular systems.

Recently, Masihi et al. (2006c), have shown that it is possible to account for moderate anisotropy in finite size scaling within percolation by first using the apparent threshold $\tilde{p}_c$ in the principal coordinate directions of the anisotropy as the value of p when 50% of realizations connect in that direction instead of the infinite percolation threshold and then rescaling with the effective length L_x as,

Percolation in Porous Media, Fig. 8

An anisotropic fracture network ($l = 5$) at the threshold with random orientation in the range $\theta \in (-30^\circ, 30^\circ)$ around the horizontal showing the *easy* direction for connection along x -axis with 3802 fractures where the percolating cluster consists of 432 fractures. Connectivity along the y -axis, which is the *difficult* direction for connection, needs much more fractures to be placed in the regions



$$P(p, L_x, \omega) = L_x^{-\beta/\nu} \mathcal{I}[(p - \tilde{p}_c) L_x^{1/\nu}] \quad (8)$$

$$\Delta(p, L_x, \omega) = \omega^{1/2} L_x^{-\beta/\nu} \Re[(p - \tilde{p}_c) L_x^{1/\nu}] \quad (9)$$

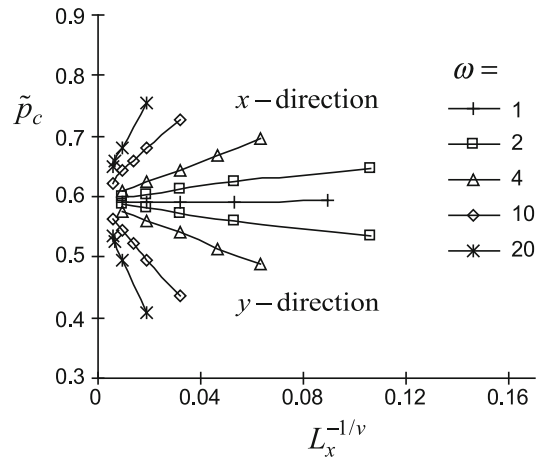
where the aspect ratio $\omega = L_x/L_y$ represents the anisotropy. The apparent threshold in each direction is given by,

$$\tilde{p}_c^i = p_c^\infty + \Lambda_i(\omega) L_x^{-1/\nu} \quad (10)$$

which has a symmetry property (see Fig. 9) where the constant of proportionality is $\Lambda(\omega) = c(\omega^{1/\nu} - 1)$ with $c \approx 0.92, 0.58$ and 0.41 for respectively elongated lattice (Masihi et al. 2006c), anisotropic fracture model (Masihi et al. 2007) and anisotropic sandbody model (Nurafza et al. 2006a, b). This means that we can use the same isotropic universal curves ($\mathcal{I}$ and $\Re$) for predicting connectivity of anisotropic cases.

Size Distribution

Another key parameter affecting the connectivity is the size distribution. In reality the sandbodies,



Percolation in Porous Media, Fig. 9 Plot of apparent threshold in both the x and the y directions of anisotropic lattices as a function of $L_x^{-1/\nu}$, showing that the shift in the apparent thresholds is symmetrically placed about the isotropic case ($\omega = 1$)

for example, may have different sizes based on the sedimentological environment in which the sands were deposited. Also, fractures usually have a length distribution depending on the degree of rock deformation (e.g. Rives et al. 1992) from

negative-exponential and log-normal to power-law distributions (e.g. Bonnet et al. 2001; Heffer and Bervan 1990; Odling et al. 1999; Segall and Pollard 1983; Van Dijk et al. 2000).

The analysis of the connectivity based on finite size scaling that we have discussed so far assumes that objects (i.e. fractures or sandbodies) all have the same lengths. However the distribution of sizes introduces a new complication. The idea behind the finite size scaling is that the percolation behavior is controlled by two dimensionless lengths, the system size, L , and the correlation length, ξ (these are made dimensionless by scaling with the linear dimension of the geometrical object). If there is a distribution of lengths then this is changed. One might expect that the connectivity behavior of such a system with a distribution of lengths is identical to the connectivity behavior of a system with constant-length objects whose object length (called the effective length, l_{eff}) can be defined in an appropriate way. In the case of fracture model, for example, using the concept of effective length introduced by Robinson (1983, 1984) and Balberg et al. (1984), the two previously determined universal connectivity curves for the constant length fractures ($\mathfrak{J}$ and $\mathfrak{R}$) can be applied to fracture systems with a distribution of fracture lengths. This representative length can be based on either the first moment $\langle l \rangle$ or the second moment $\langle l^2 \rangle$ of the fracture length distribution (Balberg et al. 1984; Berkowitz 1995; Bour and Davy 1997; Masihi et al. 2006a; Mourzenko et al. 2005; Robinson 1983; Rossen et al. 2000). From numerical studies Masihi et al. (2006a) found that the second moment gave a better fit to the data. In the case of very wide distribution of lengths (i.e. power law) the scaling exponents may be different from the standard values as there is a possibility for a single large fracture to connect both sides of the system and dominates the connectivity. In other words, in this case there is a break down in universality for the critical exponents. The dependency of the scaling exponents of percolation theory on the exponent of power law length distribution has been investigated numerically (Bour and Davy 1997; Masihi et al. 2006a).

Orientation Distribution

In reality the sandbodies, for example, are not all aligned in one direction and are affected by the depositional process. Note that the orientational disorder of the bodies which is more relevant in three dimensions can greatly enhance the connectivity of the system, particularly for the systems with thin long bodies. In percolation terminology this is a reduction in threshold which is not due to the finite size effects but a real shift in the infinite threshold. Very thin and long bodies, for example, if they are aligned they will not intersect so $p_c \approx 1$ otherwise if they have an angular dispersion they will intersect at any fractional concentration and so $p_c = 0$. There will also be another shift in apparent percolation due to finite size effects. Nurafza et al. (2006a, b) studied these effects numerically and showed that the only effect of the orientational disorder is to make the bodies appear a bit larger than they are and a bit less elongated. They defined a new aspect ratio and used the reduced percolation thresholds to account for the effects of orientation of sandbodies within the finite size scaling laws which makes the previously determined universal curves applicable for orientated sandbodies.

Spatial Correlation

The models discussed so far assumed the objects are distributed randomly and independently in the region (Poisson statistics). This is somehow in contradiction with the known existence of, for example, fracture sets or observed spatial correlation between natural fractures over scales (e.g. Bonnet et al. 2001). A survey of the literature shows that there has been little investigation of the percolation properties of systems with short- and long range correlations. Harter (2005) has shown that the percolation threshold in Markov chain random field with short range correlation decreases as the correlation scale increases but the critical exponents are unaffected (they belong to the same universality class as uncorrelated percolation). For systems with long range correlations, on the other hand, it has been shown that the percolation behavior is drastically changed as even the critical exponents may become different (Prakash et al. 1992; Schmittbuhl et al. 1993).

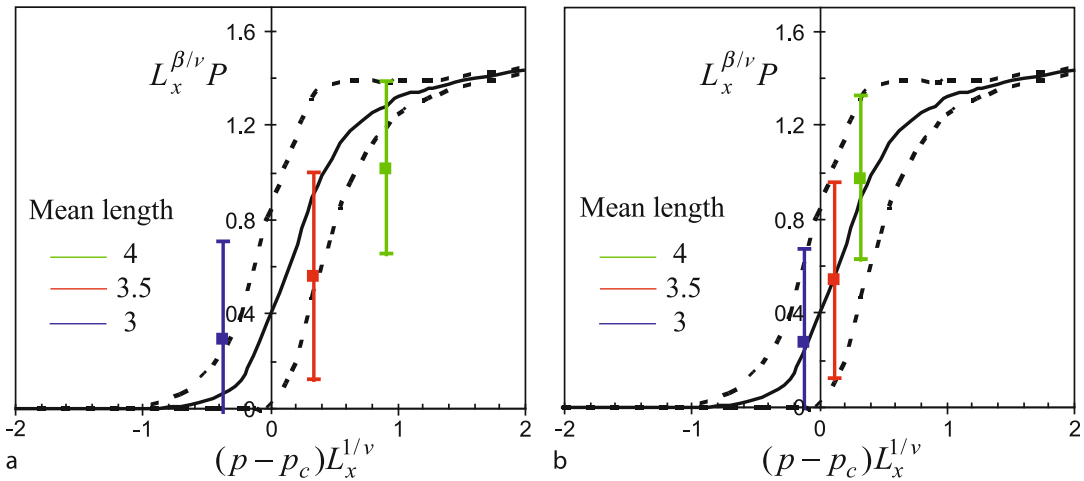
In the study of fracture networks an investigation of the spatial correlation of fractures has concentrated on the long range fracture density correlations modeled by fractal geometry (Berkowitz et al. 2000; Darcel et al. 2003c; De Dreuzy et al. 2004; Watanabe and Takahashi 1995) showed that the correlation pattern is likely to affect the connectivity behavior. When dealing with fracture correlation it is not straightforward to find the right percolation parameter p which is able to measure the connectivity of the fracture network. As pointed out by Darcel et al. (2003c) neither the mean fracture density $\rho = N^2/L^2$, proposed by Bour and Davy (1997), nor the mean fractal fracture density $\rho_D = N^D/L^D$, suggested by Berkowitz et al. (2000) are able to represent the connectivity state of constant-length fractal fracture networks. Darcel et al. (2003c) also emphasized that the transition width at the threshold for a large system with fractal correlation remains fixed (it does not vanish) which is in contrast to the second order phase transitions of percolation theory. Masihi and King (2007) have presented a model of fractures which used a simulated annealing algorithm (with an objective function defined by the spatial correlation in the displacement of fractures) to generate realizations of correlated fracture networks and then used them in the percolation approach to investigate the effects of fracture spatial correlation. They have found that the scaling exponents of the connectivity are different from the conventional, uncorrelated values (see Masihi and King 2007; Masihi et al. 2006a for more details).

With this background we now describe the percolation framework to model field scale reservoirs. We start with conventional reservoirs. Hydrocarbon reservoirs have a complicated geometry due to the complex sedimentary processes deposited them over the years. They consist of good sandstone (i.e. high permeability and porosity) containing oil within their pores, and poorer siltstones, mudstones and shales (i.e. low permeability). The main flow of oil during recovery is through these good sands and flow through poorer rock being too slow to be of economic consequence. Hence, connectivity of these sandbodies (also called flow units) across the

reservoir or in between an injection and a production well is crucial. Note that the total sands gives the total oil in place and the fraction of connected sands between two wells shows the expected recoverable oil between the two wells. A part of the connected sand fraction is dead end and cannot contribute to the flow. The flowing part (backbone) of connected sands controls the flow through sands and so affects the effective permeability, sweep efficiency and breakthrough and post break through time behavior. Many important decisions for a given field can be made based on the knowledge of the connectivity and conductivity of these flow units. For example, at the exploration and appraisal stage, decisions about initial well spacing and location can be made based on oil volumes connected by the wells and recovery factors; during plateau phase the decision about the end of plateau and the rate of increases of water or gas ratios depends on the knowledge of the geometry of the backbone or during the decline phase decisions about targeting infill wells to extend field life will be based on volumes of unswept oil or uncontacted oil.

The conventional approach to address these entails building detailed reservoir models which is very expensive in terms of human and CPU times. It has long been understood that flow in heterogeneous porous media is largely controlled by continuity of permeability contrasts, either flow barriers (e.g. shales or high permeability streaks) or faults. Although there are other influences these are the predominant features affecting flow. With this in mind we look to model reservoir flow which concentrates on the connectivity of permeability contrasts (Fig. 10).

Imagine a typical reservoir model constructed with an object-based technique (Deutsch 2002). That is, geometrical objects (representing geological entities, e.g. shales, fractures, sand bodies etc.) are placed randomly in space. For example, the reservoir may have been deposited by meandering river belts in which case the good sand occurs as packages in a low permeability background. Then the connectivity and conductivity can be estimated directly by percolation theory. Note that the net to gross ratio is the volume fraction of the good sand and is, therefore,



Percolation in Porous Media, Fig. 10 A comparison of connectivity scaling of three correlated fracture networks with the average fracture length 4, 3.5 and 3 with the universal connectivity curves (solid and dotted curves are

P and $P \pm \Delta$) using: a standard values for the exponent ($1/\nu = 0,75$ and $\beta/\nu = 0,105$) and b modified values $1/\nu = 0,4$ and $\beta/\nu = 0,09$

identical to the occupancy probability p . Suppose we have a reservoir of size L and a pair of wells separated by a Euclidean distance r . We can ask questions about the probability that the two wells are connected, or in percolation terminology, in the same cluster. This is just the two point correlation function defined previously. Suppose we want to know what fraction of the sand in contact with the wells is connected to both wells. This is just the connectivity function P defined earlier. We can use finite size scaling to estimate this fraction. Also, we can use related scaling laws to estimate the uncertainty. Note that these are algebraic laws with no spare parameters. The percolation threshold is defined by the shape of the objects, but it is largely unimportant whether we model the sand units as rectangles or ellipsoids or other shapes (provided they are not too exotic). The scaling laws and exponents are determined from lattice models (and this has been done very extensively in the literature) and can be straightforwardly applied.

The percolation framework can be used to find the probability distribution for the breakthrough time for convection of a single phase passive tracer between an injector and a producer. Comparison of preliminary results (Andrade et al. 2000; Dokholyan et al. 1998; King et al. 2001;

Lee et al. 1999) showed that the agreement between prediction from scaling law and the numerical simulation which is good enough for engineering purposes given the fact that the prediction from the scaling law took a fraction of a second of CPU times compared with the hours required for the conventional detailed simulation. Having estimated the breakthrough time, Roslien et al. (2004) showed that log-log plot of the mean and variance in production results condition to any breakthrough time t_{br} against $(t - t_{br})$ will lie on top of each other to produce two universal curves. Now with these master curves, one can make a rapid estimate of the mean and variance in future production (e.g. the time taken for production to fall by 50% or water cut to increase to 50%) good enough for engineering purposes.

In fractured reservoirs with low matrix permeability the flow behavior depends strongly on the spatial distribution of the fractures. In this case, the fractures are the flow units which need to be distributed randomly in the impermeable background (i.e. matrix). Then again the connectivity and conductivity can be estimated directly by percolation theory. The occupancy p can be interpreted as the density of fractures e.g. number density or the critical fracture length necessary to ensure percolation for a given

number of fractures in a domain (Pike and Seager 1974). Equivalent terms to this can be volumetric base (i.e., average number of fractures in the region), topological base (Adler and Thovert 1999) (i.e., average number of connections with surrounding fractures) or a combination (Masihi et al. 2006b) based on average excluded area i.e., the area around a fracture in which the center of another fracture must lie in order for them to overlap over the distribution of the fracture orientation and (Balberg et al. 1984) length. Extensive studies have shown that constant-length fracture models belong to the general universality class of continuum percolation systems (Balberg et al. 1983; Berkowitz 1995; Bour and Davy 1997; Bour and Davy 1998; Charlaix 1986; Robinson 1984). Recently, Belayneh et al. (2006) have applied scaling laws from percolation theory to predict the connectivity of mineralized fractures with length distribution exposed on the southern margin of the Bristol Channel Basin.

Future Directions

There is obviously a need for further development to turn many concepts involved in this article into practical application. One area is to look for connectivity between two wells (represented by points or lines in 2D and 3D, respectively) similar to the previous works on the structure of the cluster connecting two given sites or lines of a 2D and 3D lattices (Barthelemy et al. 1999; Da Silva et al. 2003). Clearly the connectivity between two points will be lower than that between two sides. In determining the connectivity between two points the correlation function, $g(r)$ defined previously has a major role.

Percolation can do more than predict static connectivity. There are scaling laws for the effective permeability $K_{\text{eff}}(p - p_c^\infty)^\mu$ for infinite size systems where the conductivity exponent μ is about 1.3 and 2 in two and three dimensions respectively (Stauffer and Aharony 1992). It is clear that only a subset of the percolating cluster (called the backbone) can be swept whereas the dead ends are stagnant. It would be expected to see a similar finite size scaling and anisotropy

effects to those for the connectivity. However, the detailed development for this is computationally very demanding as it requires solving the flow equations.

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Percolation, Faults and Fractures in Rock

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Article Outline

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Glossary

Dimensionless density The dimensionless density is the number of objects per excluded volume.

Excluded volume The *excluded volume* V_{ex} of an object is defined as the volume surrounding it, in which the center of another object must be in order for them to intersect.

Fracture network A fracture network is generally defined as a set of individual fractures which may or may not intersect.

Percolation and percolation threshold Percolation is defined as the existence of a spanning connected cluster in the fracture network. Percolation occurs when the number of fractures per unit volume is equal or larger than a certain value called the percolation threshold.

Plane convex fractures A plane fracture is convex if for any points A and B which belong to

the fracture, all the points of the segment AB belong to the fracture.

Definition of the Subject

The study of fractured porous media is of great practical and theoretical importance. It has been first generated by the fact that the presence of fractures can change completely the macroscopic properties of porous media which are present for instance in oil reservoirs, aquifers or waste repositories. The first contributions to this subject were made from very different standpoints by Barenblatt and coworkers (1960), Conrad and Jacquin (1973), and Witherspoon and coworkers (see for instance (Long et al. 1982)).

In the eighties, these studies were renewed by concepts such as percolation and fractals. Fracture networks were first addressed in the framework of continuum percolation by Charlaix et al. (1984) and Balberg (1985).

Since the mid nineties, important progress have been made in this field thanks to systematic numerical experiments which can be rationalized by using the concept of excluded volume.

Introduction

Knowledge of geometrical properties of fracture networks is crucial to the understanding of flow and other transport processes in geological formations, both at small and large scales; introduction of fractures in a porous rock matrix seriously alters the macroscopic properties of the formation. Moreover, studies of fracture geometries during the last 30 years show that naturally occurring geological fractures exist on scales ranging from a few mm to several kilometers (Sahimi and Yortsos 1990). Therefore, fracture networks are likely to influence the transports on a large range of scales. Because of their importance, fracture networks are studied and applied in various areas

such as oil and gas recovery, hydrology, nuclear waste storage and geothermal energy exploitation.

Geological fractures can be defined as discrete discontinuities within a rock mass; these breaks are characterized by the fact that their local aperture (defined as the local distance between the two surfaces which limit the fracture) is significantly smaller than their lateral extent; in other words, when they are viewed from far away, fractures can be assimilated to surfaces of discontinuity; in most cases, these surfaces are relatively plane. Fractures have varying degrees of aperture, and may in some cases be completely closed either because of deposition of material induced by fluid flow, or by displacements of the matrix.

An important property of these fracture sets or fracture network is their connectivity and their percolation properties. If a network percolates, fluid can circulate only through it and most likely much more rapidly than in the surrounding porous medium itself. Connectivity studies of fracture networks were initiated in 3D by Charlaix et al. (1984) and Balberg (1985).

The purpose of this chapter is to provide a complete and updated view of the percolation properties of fracture networks in rocks. It is organized as follows. In section “[Fracture Networks](#)”, fractures are modeled as plane convex polygons which enables the introduction of the concept of excluded volume V_{ex} . This volume is a simple function of the surface and perimeter of the fractures, and it enables to introduce a dimensionless fracture density ρ' which is defined as the number of fractures per excluded volume. The tools necessary for the numerical study of the percolation thresholds are detailed and applied to mono- and poly-disperse fracture networks. It is shown that when expressed in terms of ρ' , the percolation threshold does not depend anymore on the fracture shapes. This crucial property is presented and discussed.

Section “[Determination of the Dimensionless Density from Experimental Data](#)” is devoted to the determination of the dimensionless density from experimental data. In most cases, these data are based on 1D and 2D measurements of fracture traces along boreholes or on exposed outcrops. These measurements necessitate extrapolation by stereological techniques to three dimensions.

Significant progress can be made for plane convex fractures. Some recent applications of the methodology are given.

Finally, the independence of the dimensionless percolation threshold on the fracture shape can be extended to other properties such as other geometric properties and the macroscopic permeability of fractured rocks. These extensions are summarized in section “[Role of the Dimensionless Density in Other Geometrical Properties and Permeability](#)”.

Fracture Networks

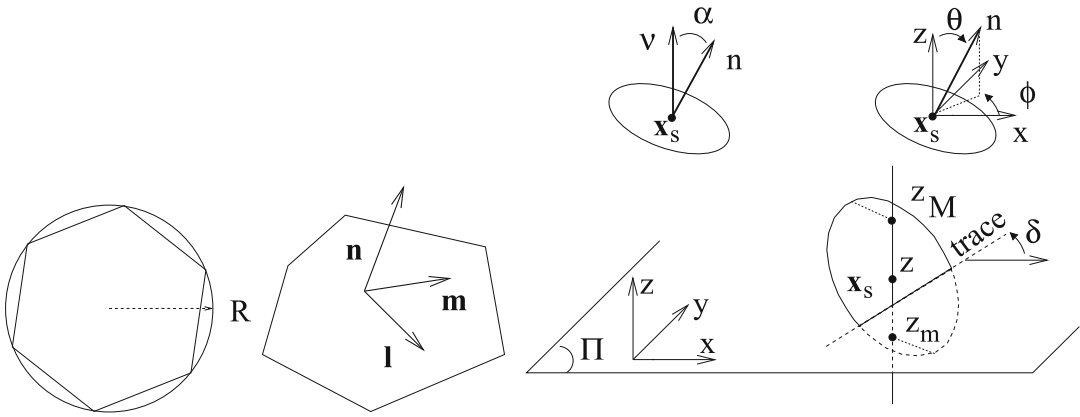
A fracture network is generally defined as a set of individual fractures which may or may not intersect.

On a scale large with respect to the fracture aperture, fractures are usually modeled as convex, finite polygons possibly based on an embedding disk as shown in Fig. 1a. This is only a simplifying assumption which however provides a standard starting point for studying fracture networks. Convex polygons can be used to analyze shape and area dependencies of geometrical and topological features in the fracture systems in a systematic way.

The individual fractures are characterized by their orientation. This orientation is usually given by two unit vectors $\mathbf{n}$ and $\mathbf{m}$ (cf. Fig. 1). $\mathbf{n}$ is the normal to the fracture plane; $\mathbf{m}$ gives the orientation of the polygon in the fracture plane.

The simplest model consists of a network in which all fractures have the same shape and are inscribed in a circle with a given radius R . The normal vectors $\mathbf{n}$ are uniformly distributed on the unit sphere. The density ρ of this isotropic mono-disperse network is defined as the number of fractures per unit volume. An illustration of such a fracture system is shown in Fig. 2a.

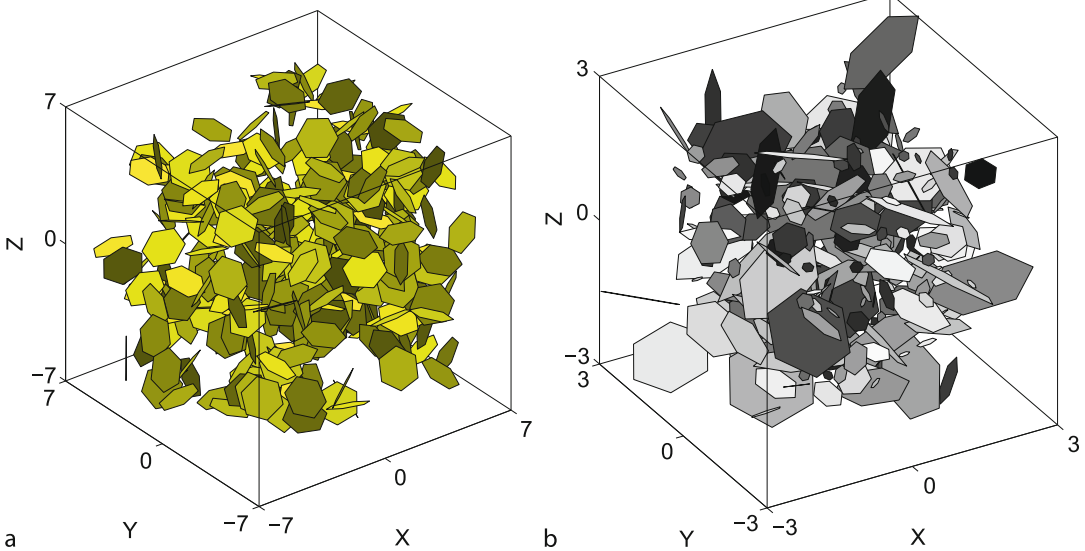
Next consider three-dimensional networks made up of polydisperse fractures with plane polygonal shapes. These polygons may be regular or not, but all their vertices are supposed to lie on their circumscribed circle, whose radius R provides a measure of their size. In agreement with many observations of fractured rocks (Adler and Thovert 1999), the statistical distribution of the fracture sizes is supposed to be given by a power law



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Fig. 1 Notations. Convex polygons such as hexagons are created within a circle of radius R (a). This polygon requires two unit vectors n and m to be oriented in space

(b); l is a unit vector perpendicular to n and m . (c) illustrates the notations which are mostly used in section “[Determination of the Dimensionless Density from Experimental Data](#)”



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Fig. 2 Examples of three-dimensional fracture networks. (a) Monodisperse network made of identical polygons. The volume of size L^3 contains 495 hexagons; $L = 12R$ where R is the radius of the circle in which the hexagon is

inscribed. (b) Polydisperse network of hexagonal fractures, with $L' = 4$, $a = 1.5$, $R'_m = 0.1$, which contains $N_{fr} = 300$ fractures ($\rho'_{21} = 1.25$, $\rho'_3 = 2.44$). The unit for the coordinates is R_M

$$n(R) = \alpha R^{-a} \quad (1)$$

where $n(R)dR$ is the probability of fracture radii in the range $[R, R + dR]$; α is a normalization coefficient, and the exponent a ranges between 1

and 5. In practice, R may vary over a large interval which can span five orders of magnitude, from the size R_m of the microcracks to the size R_M of the largest fractures in the system. The normalization condition implies that α verifies

$$\alpha = \frac{a-1}{R_m^{1-a} - R_M^{1-a}} \quad (a \neq 1);$$

$$\alpha = \frac{1}{\ln R_M - \ln R_m} \quad (a = 1). \quad (2)$$

The definition of the network density ρ for polydisperse networks should be modified. To this end, we introduce the volumetric number density of fracture per fracture size $F(R)$,

$$F(R) = \rho n(R) \quad (3)$$

where $F(R)dR$ is the number of fractures with radius in the range $[R, R + dR]$ per unit volume.

An example of such polydisperse networks is given in Fig. 2b.

Percolation of Fracture Networks

General Considerations on Continuum Percolation

Continuum Percolation Percolation, i.e., the existence of a spanning connected cluster in the fracture network, is a crucial topological property which conditions many other geometrical or transport properties of the network.

Percolation of discrete sites or bonds lattices has been closely studied (see, e.g. Sahimi 1995; Stauffer and Aharony 1994). In these lattices, the sites or bonds are occupied with a probability p , which can be interpreted as a concentration. In large systems, percolation occurs when p exceeds a critical value p_c , known as the percolation threshold, which depends on the underlying lattice structure. For p close to p_c , however, many geometrical or transport coefficients are known to scale as power laws of the difference $p - p_c$, according to the standard form

$$X \propto (p - p_c)^\alpha. \quad (4)$$

The quantity X may represent the correlation length, the fraction of sites connected to the infinite cluster, or the conductivity of the system. Different exponents are associated with the various quantities, but each is generally believed to be

universal, i.e., insensitive to the details of the underlying lattice.

It is, of course, tempting to try to transpose this theoretical framework to the problem at hand. It is intuitively obvious that a fracture network will start percolating if some critical concentration is reached. The main difficulty is to define an equivalent of the probability p in discrete lattices. As shown below, this can be done by using the concept of excluded volume, introduced by Balberg et al. (1984) in the context of fracture networks.

Fracture networks belong to the general class of continuum percolation systems. Applications of continuum percolation concepts to geophysical problems have been reviewed by Berkowitz and Ewing (1998). Continuum percolation differs from lattice percolation in several respects. First, the occupancy probability p in a discrete lattice ranges between 0 and 1, which means that there is a maximal concentration; the filling of the system can be defined relative to this upper bound. In continuum percolation, there is generally no such upper bound. For instance, there is ideally no upper limit to the degree of fracturation of a piece of rock. Consequently, the relative concentration p has to be replaced by a volumetric density. Second, any site or bond in lattice percolation cannot have more than a maximum number z of neighbors, called the lattice coordination number, whereas there is no limitation to the number of intersections for a fracture in a network. Other differences result from the variable lengths and orientations of the bonds, in contrast with the discrete set of values imposed by a lattice, which may be significant for transport properties (see Balberg 1987).

Note that in this section we only consider “large” systems, i.e., the size of the objects in the percolation system may have a broad distribution, but the overall domain extension is supposed to widely exceed the size of the largest objects it contains. This condition may sometimes be difficult to fulfill; natural fracture networks often involve largescale faults, which may in themselves ensure percolation if they cross the domain of investigation. Bour and Davy (1997) and later Mourzenko et al. (2004b) considered such broad size-distributions where the probability of a spanning single fracture is non-zero.

In view of the previous considerations, two definitions of the system concentration appear possible. One is volumetric, quantified by the average number of objects in a reference volume; the other is topological, defined as the average number of connections with surrounding objects. These two definitions are nicely reconciled by the introduction of the concept of excluded volume.

The *excluded volume* V_{ex} of an object was defined by Balberg et al. (1984) as the volume surrounding it, in which the center of another object must be in order for them to intersect. We first discuss the simplest case of populations of identical objects, with volume V . For example, the excluded volumes of a sphere with volume V in 3D and of disks with area A in 2D are

$$\begin{aligned} V_{\text{ex}} &= 8V & \text{for spheres;} \\ A_{\text{ex}} &= 4A & \text{for disks in the plane.} \end{aligned} \quad (5)$$

These equations are also valid for any object with convex shape, if all the objects in the population have identical orientations.

If the objects are anisotropic and have distributed orientations, the excluded volume has to be averaged over all possible relative orientations of the intersecting objects.

Now suppose that the volumetric density of objects per unit volume is ρ . It is natural to use V_{ex} as a reference volume, and we may define the dimensionless density ρ' as the number of objects per volume V_{ex}

$$\rho' = \rho V_{\text{ex}}. \quad (6)$$

On the other hand, the definition of V_{ex} implies that ρ' is also the average number of intersections per object, if they are randomly located according to a Poisson process. Therefore, given the shape of the object and its orientation distribution (and thus V_{ex}), the definition (6) incorporates both the volumetric and topologic aspects mentioned above.

It should be emphasized however, that the definition of the excluded volume is meaningful only if the object locations are uniformly distributed in space. If there are spatial correlations, they should be replaced by a spatial integral of the pair separation distribution function (see for instance (Drory et al. 1997) for applications to the physics of liquids).

Calculation of the Excluded Volume for Plane Convex Fractures A general expression for the excluded volume was established very early in the context of statistical mechanics by Isihara (1950), for isotropically oriented objects. For two three-dimensional convex objects A and B with volumes V_A and V_B , areas A_A and A_B and surface averaged mean radius of curvature R_A and R_B , Isihara (1950) obtained the mutual exclusion volume

$$V_{\text{ex},AB} = V_A + V_B + (A_A R_B + A_B R_A). \quad (7)$$

This expression can then be averaged over the distributions of object shapes and sizes. For equal spheres, Eq. (5) is obtained. For flat convex objects randomly oriented in space with perimeters P_A and P_B , it is reduced to Charlaix et al. (1984)

$$V_{\text{ex},AB} = \frac{1}{4} (A_A P_B + A_B P_A). \quad (8)$$

On averaging (8) over the size distribution of objects with identical shapes, one obtains

$$V_{\text{ex}} = \frac{1}{2} \langle A \rangle \langle P \rangle \quad (9)$$

where $\langle \cdot \rangle$ is the statistical average. If A and B are identical, (9) yields

$$V_{\text{ex}}^{\text{iso}} = \frac{1}{2} A P. \quad (10)$$

If the population of polygons is not isotropic and has a probability distribution $n(f)$, which may involve the shape or the size of the polygons, the average of (8) yields

$$V_{\text{ex}}^{\text{iso}} = \frac{1}{4} \int \int n(F_1) n(F_2) (A_1 P_2 + A_2 P_1) dF_1 dF_2$$

$$= \frac{1}{2} \langle A \rangle \langle P \rangle \quad (11)$$

where $\langle A \rangle$ and $\langle P \rangle$ are the average area and perimeter. Alternatively, the polygon orientation may be incorporated into $n(f)$ and a general expression of V_{ex} can be obtained.

Determinations of Continuum Percolation Thresholds The percolation thresholds of various simple continuous systems have been determined, since the pioneering papers of Sher and Zallen (1970) and Pike and Seager (1974). These early works were reviewed by Balberg et al. (1984) and Balberg (1987). A few examples are given in Table 1, for monodisperse objects in a d -dimensional space. The critical concentration is described in terms of the average number ρ'_c of connections per object.

The influence of the orientation distribution was investigated by Robinson (1983, 1984) and Balberg et al. (1984). For sticks with constant length in the plane (Robinson 1983) has shown that ρ'_c is identical for uniform orientation distributions in any angular sector and equal to the value 3.6 for an isotropic distribution. On the other hand, the value 3.2 for orthogonal sticks is also valid for any bimodal orientation distribution. By considering three-dimensional systems (Balberg et al. 1984), also conclude that the total excluded volume at percolation is independent of

the degree of anisotropy. Balberg (1985) proposed a set of bounds which correspond to orthogonal and parallel object systems

$$\begin{aligned} 3.2 \leq \rho'_c \leq 4.5 \quad d = 2; \quad 0.7 \leq \rho'_c \\ \leq 2.8 \quad d = 3. \end{aligned} \quad (12)$$

All these results were obtained by numerical simulations. One should also mention the heuristic criterion developed by Alon et al. (1991). They define the average “bonding distance” l as the mean distance between connected objects, which is essentially the gyration radius of the excluded volume

$$l^2 = \frac{1}{V_{\text{ex}}} \int_{V_{\text{ex}}} r^2 d^3 \mathbf{r}. \quad (13)$$

Note that l does not depend on the density of objects. They then postulate that percolation occurs when the average distance L_d between objects with at least two neighbors is smaller than or equal to $2l$. To evaluate L_d , they note that the number k of connections to a given object corresponds to a Poisson distribution

$$\text{Pr}(k) = \frac{\rho'^k}{k!} e^{-\rho'}. \quad (14)$$

Therefore, the density ρ_2 of objects with at least two neighbors is

$$\rho_2 = \rho \left[1 - (1 + \rho') e^{-\rho'} \right]. \quad (15)$$

Percolation, Faults and Fractures in Rock, Table 1 Thresholds ρ'_c for various continuum percolation systems in d dimensions

d	Object type	ρ'_c	d	Object type	ρ'_c
2	Orthogonal sticks	3.2	3	Orthogonal elongated rods	0.7
2	Randomly oriented sticks	3.6	3	Randomly oriented elongated rods	1.4
2	Disks or parallel objects	4.5	3	Orthogonal squares	2.0
			3	Randomly oriented squares	2.46
			3	Spheres or parallel objects	2.80

Thus, an estimate of L_d follows from

$$\frac{4}{3}\pi\left(\frac{L_d}{2}\right)^3 = \frac{1}{\rho_2}. \quad (16)$$

An equation for the critical concentration ρ'_c can be directly deduced from the statement that $L_d = 2l$. Although the argument is not substantiated, it is quite successful. It yields directly $\rho'_c = 2.80$ for spheres. In two dimensions, L_d is replaced by the average distance between objects with at least 5 neighbors.

An interesting feature of this argument is that it can be easily generalized to account for spatial correlations. If $\rho g(r)$ denotes the probability density of finding an object center at a distance r from an object located at the origin, the bonding distance is defined by the weighted average

$$l^2 = \frac{\int_{V_{\text{ex}}} r^2 g(r) d^3\mathbf{r}}{\int_{V_{\text{ex}}} g(r) d^3\mathbf{r}}. \quad (17)$$

Similarly, the average number of bonds per object appears as

$$\rho' = \rho \int_{V_{\text{ex}}} g(r) d^3\mathbf{r}. \quad (18)$$

Using these two definitions, an equation for ρ'_c can be obtained. Its predictions were successfully compared by Alon et al. (1991) to numerical simulations for systems of hard-core spheres with or without interaction potentials.

Only monodisperse objects have been addressed so far in this subsection. For polydisperse populations, there seems to be some confusion in the literature. For flat objects, the statistical derivation of the excluded volume in section “Calculation of the Excluded Volume for Plane Convex Fractures” quite naturally yielded the averages (9) or (11), which account for the sizes of the two intersecting objects. For isotropic populations of segments with length l in the plane or disks with radius R in space, for instance, the averages can be expressed as

$$V_{\text{ex}} = \frac{2}{\pi} \langle l \rangle^2 \quad \text{segments, } d = 2 \quad (19a)$$

$$V_{\text{ex}} = \frac{\pi^2}{8} \langle R \rangle^2 \langle R \rangle \quad \text{disks, } d = 3. \quad (19b)$$

However, another type of average has been proposed by Balberg et al. (1984), namely,

$$W_{\text{ex}} = \frac{2}{\pi} \langle l^2 \rangle \quad \text{segments, } d = 2 \quad (20a)$$

$$W_{\text{ex}} = \frac{\pi^2}{8} \langle R^3 \rangle \quad \text{disks, } d = 3. \quad (20b)$$

On the basis of the numerical simulations of Robinson (1983, 1984), Balberg et al. (1984) and others claim that the average bond number for polydisperse objects is not given by Eq. (6) but instead by

$$\rho'' = \rho W_{\text{ex}}. \quad (21)$$

However, a careful examination of Robinson's (1983) data shows that they correspond very accurately to Eq. (6) with (19a). Finally, the derivations of Berkowitz and Adler (1998) are based on (19b) and yield consistent results.

Actually (Robinson 1983, 1984) showed that ρ'_c is not invariant for similar systems of segments in the plane with various degrees of polydispersity, while ρ''_c is. Bour and Davy (1997) also observed that ρ''_c is roughly constant for very broad power-law segment size distributions. The profound meaning of this observation is that continuum percolation is not determined only by the average coordination, when connections over various ranges may coexist. As suggested by Rivier et al. (1985), this is probably because contacts between objects too close to each other are redundant to percolation.

To summarize, the density ρ' based on V_{ex} resulting from the averages (9), (11), or (19a) is always equal to the mean number of intersections per object, but it cannot be used to relate the percolation thresholds of mono- and polydisperse systems. The alternative definition ρ'' in (21) is very successful in this respect and is going to be generalized as ρ'_3 in (29).

Methods

The three main tools necessary for the numerical study of the percolation properties of the fracture network models are summarized in this section.

First, the medium is assumed to be spatially periodic on a large scale. A detailed description of spatially periodic media is given by Adler (1992),

and only the main characteristics of these models are briefly repeated here. The geometrical and physical properties of the system under investigation are invariant under the translations

$$\mathbf{R}_i = i_1 \mathbf{l}_1 + i_2 \mathbf{l}_2 + i_3 \mathbf{l}_3 \quad (22)$$

where $\mathbf{i} = (i_1, i_2, i_3) \in \mathbb{Z}^3$, and where $\mathbf{l}_1, \mathbf{l}_2$ and $\mathbf{l}_3$ define a unit cell where the system is studied. The entire space is tiled by replicas of this unit cell, translated by $\mathbf{R}_i$. All the studies presented in this chapter are performed in cubic unit cells where $|\mathbf{l}_1| = |\mathbf{l}_2| = |\mathbf{l}_3| = L$.

Spatial periodicity implies that fractures may cross the imaginary unit cell boundaries, and reach the neighboring cells of the periodic medium. Therefore, for polydisperse fractures, R_M should be at least smaller than $L/2$. Moreover, in order to represent a homogeneous medium by a periodic model, one has to set the unit cell size much larger than any finite characteristic length scale in the system. Practically speaking, because of the finite size effects which will be discussed in section “Methods”, R_M is at least smaller than $L/4$.

Second, the networks are characterized by a graph which provides all the necessary relations and information. This graph, denoted by Γ_1 , consists of vertices which correspond to the polygons, and edges which correspond to the intersection between polygons. Γ_1 will be used to study network percolation as a function of fracture shape, distribution and density, as well as to characterize the topological features of the percolating components of the networks.

The information relative to the intersections is stored in the graph Γ_1 . Since the networks considered here are spatially periodic, intersections of a polygon P_1 with the periodic replicas of a polygon P_2 in the 26 neighboring unit cells have to be checked as well. Once the intersections have been identified, the edges of Γ_1 are known, and Γ_1 can be set up.

Third, in order to estimate the percolation thresholds, the classical finite-size scaling method described in Stauffer and Aharony (1994) is used. The percolating system is studied for various cell sizes L . For given values of L and ρ , the probability $\Pi_L(\rho)$ of having a percolating cluster is derived from numerous realizations of the system. Then, the numerical data are used to estimate ρ_{Lc} (the

value for which $\Pi_L(\rho) = 1/2$) and an estimate of the width Δ_L of the transition region of $\Pi_L(\rho)$. $\Pi_L(\rho)$ was fitted with an error function of the form

$$\Pi_L(\rho) = \frac{1}{\sqrt{2\pi}\Delta_L} \times \int_{-\infty}^{\rho} \exp\left\{-\frac{(\xi - \rho_{Lc})^2}{2(\Delta_L)^2}\right\} d\xi \quad (23)$$

where ρ_{Lc} and Δ_L are fit parameters. Once they have been evaluated for several values of L , the asymptotic value ρ_{Lc} for infinite systems ρ_c can be derived from the two scaling relations

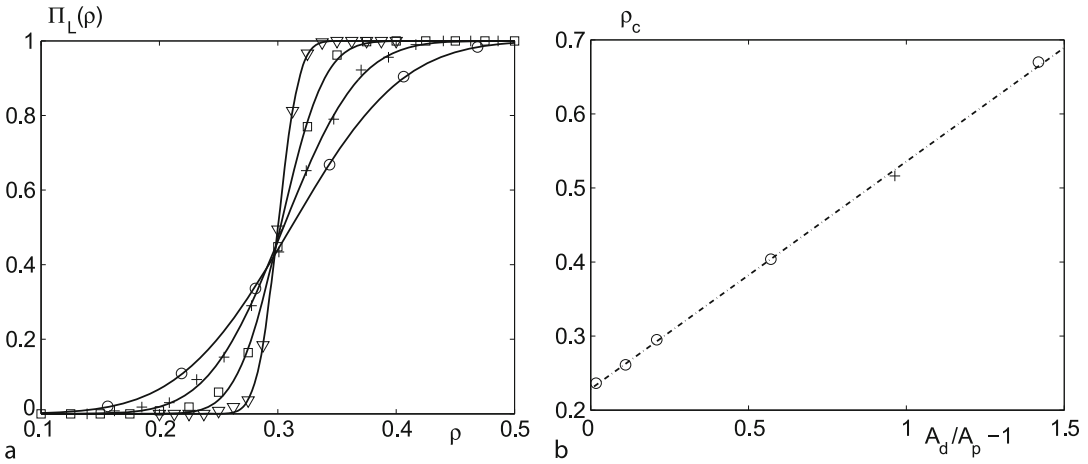
$$\rho_{Lc} - \rho_c \propto L^{-1/\nu} \quad \Delta_L \propto L^{-1/\nu}. \quad (24)$$

Monodisperse Fractures

This case was addressed by Huseby et al. (1997). Since the computer time increases proportionally to the square of the number N of objects, L (measured in units of the disk radius R) was kept below 16 in this early contribution. Despite the small cell sizes, the scaling laws (24) are well verified, which justifies the extrapolations of ρ_c at $L \rightarrow \infty$. The polygons were created, and intersections identified. Percolation was checked in all possible directions x , y and z . Periodic boundary conditions were applied to the 3d graph during this search; this means that a cluster must touch two opposite faces of the unit cell, and in addition contain fractures intersecting one another across the faces.

An example of the plots of the estimated $\Pi_L(\rho)$ data points is given in Fig. 3a, together with the fitted error functions. Plots of $\ln(\Delta_L)$ vs $\ln(L/R)$ were used to obtain the critical exponent ν . The various polygons are expected to belong to the same universality class, and ν was expected to be the same in all cases. Values were in the range $\nu = 1.011 \pm 0.044$. The plots of ρ_{Lc} vs Δ_L were extrapolated for $\Delta_L \rightarrow 0$ to find ρ_c and these extrapolations are shown in Fig. 3b as functions of the shape factor $A_d/A_p - 1$ where A_d is the area πR^2 of the circumscribed disk.

These results can be analyzed in terms of the average number of intersections per fracture ρ' . Equation (10) can be applied to networks made of identical polygons



Percolation, Faults and Fractures in Rock, Fig. 3 (a) The probability of percolation $\Pi_L(\rho)$ vs the density ρ of fractures in fracture networks created by equal sized, regular hexagons. Data are for sample sizes $L/R = 4$ (o), 6 (+),

10 ($\square$), 20 (∇). The solid lines are the fitted error functions. (b) The percolation thresholds ρ_c for regular polygons (o) and rectangles with $a/b = 0.5$ (+) vs $(A_d/A_p - 1)$. The linear fit ($- \cdot - \cdot -$) yields $\rho_c = 0.231 \pm 0.002$ for disks

$$\frac{V_{\text{ex}}}{R^3} = \pi^2 \left(\frac{N_v}{\pi} \right)^2 \cos \left(\frac{\pi}{N_v} \right) \sin^2 \left(\frac{\pi}{N_v} \right), \quad (25a)$$

(regular N_v - polygons)

$$\frac{V_{\text{ex}}}{R^3} = \frac{8a(a+1)}{(a^2+1)^{3/2}}, \quad (25b)$$

(rectangles with aspect ratio a)

The resulting values of ρ'_c are remarkably constant (cf. Huseby et al. 1997). For all the fracture networks, including the cases of anisotropic (rectangular) polygons, ρ'_c is within the range

$$\rho'_c = 2.26 \pm 0.04. \quad (26)$$

Note that (26) concurs with the limits (12) set up by Balberg (1985) for 3d systems.

To summarize, this set of numerical results suggests that the percolation threshold of a network of identical Poissonian polygons has a universal value, expressed as Eq. (26).

Polydisperse Fractures

Since natural fracture networks are likely to have more complex size and shape distributions, the extension of (26) to these cases is of great interest.

The key for this extension is the definition of a proper averaging procedure for the excluded volume.

The fracture size R is always supposed to follow the power law (1). Moreover, fractures of various shapes S are considered as well as mixtures of shapes. The three length scales R_m , R_M and L define two dimensionless ratios

$$R'_m = \frac{R_m}{R_M}, \quad L' = \frac{L}{R_M}. \quad (27)$$

Moreover, it will be shown below that global connectivity (percolation) is no longer controlled solely by the local one (mean coordination), in the case of size polydispersity, and the definition of the percolation parameter has to be generalized. Since shape effects are well accounted for by $\langle V_{\text{ex}} \rangle$, it is useful to define the dimensionless shape factor $\langle V_{\text{ex}} \rangle$, for a set of fractures with identical shapes, but possibly different sizes

$$\langle v_{\text{ex}} \rangle = \frac{\langle V_{\text{ex}} \rangle}{\langle R \rangle \langle R^2 \rangle}. \quad (28)$$

It can then be used to define two dimensionless densities, with different weightings of the fracture sizes

$$\begin{aligned}\rho'_{21} &= \rho \langle v_{\text{ex}} \rangle \langle R^2 \rangle \langle R \rangle = \rho \langle V_{\text{ex}} \rangle; \\ \rho'_3 &= \rho \langle v_{\text{ex}} \rangle \langle R^3 \rangle.\end{aligned}\quad (29)$$

The subscripts are reminders of the statistical moments of R involved in each definition. ρ'_{21} is the generalization of ρ' for monodisperse networks, since it can be shown that it is still equal to the mean number of intersections per fracture (Adler and Thovert 1999). Both ρ'_{21} and ρ'_3 reduce of course to ρ' in case of equal-sized fractures.

The main tools required to study the percolation of polydisperse networks model are similar to the ones described in section “Methods”.

For given values of the parameters, the probability Π of having a percolating cluster which spans the cell along the x -direction is derived from N_r random realizations of the system; then, the value ρ'_c for which $\Pi = 0.5$ is estimated. Π and ρ'_c depend on several parameters as summarized by the formulae

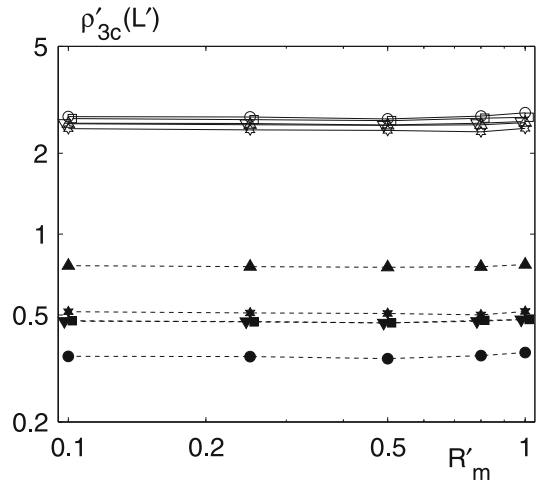
$$\Pi(R'_m, L', a, S, \rho'), \quad \rho'_c(R'_m, L', a, S) \quad (30)$$

where ρ' denotes any one of the dimensionless densities defined in (29). For brevity, they will be often written as $\Pi(L', \rho')$ and $\rho'_c(L')$.

In practice, $\Pi(L', \rho')$ was evaluated from sets of 500 realizations, for about 10 values of the network density, evenly distributed in a range where Π varies from 0.05 to 0.95. Since there is a correspondance between ρ'_{21} and ρ'_3 , for given values of S , a and R_m , the same data sets can be used to determine $\rho'_{21c}(L)$ and $\rho'_{3c}(L)$. The 95% confidence interval is estimated to be about ± 0.04 in terms of $\rho'_{3c}(L)$.

The influence on ρ'_c of the four parameters in Eq. (30) was systematically studied in Mourzenko et al. (2004b). We only state here the main result, which is that in the range $1.5 \leq a \leq 4$, $R_m \ll L$ and for (almost) any fracture shape, ρ'_c depends only on the domain size, and that in the limit of infinite domains, a unique value of $\rho'_c(\infty)$ applies in all cases. The independence on the various parameters is illustrated in the following examples.

In the example of Fig. 4, L' and a are kept constant, but the range of size and the fracture shapes varied. The networks contain hexagons,



Percolation, Faults and Fractures in Rock, Fig. 4 The percolation thresholds ρ'_{3c} (open symbols, solid lines) and $\rho_c \langle R^3 \rangle$ (black symbols, broken lines) for networks with $L' = 6$ and $a = 1.5$ for regular hexagons (o), squares (□), triangles (Δ), mixture of hexagons and triangles, 50%–50% (∇), and mixture of hexagons and rectangles with aspect ratio 4, 50–50% (⋈)

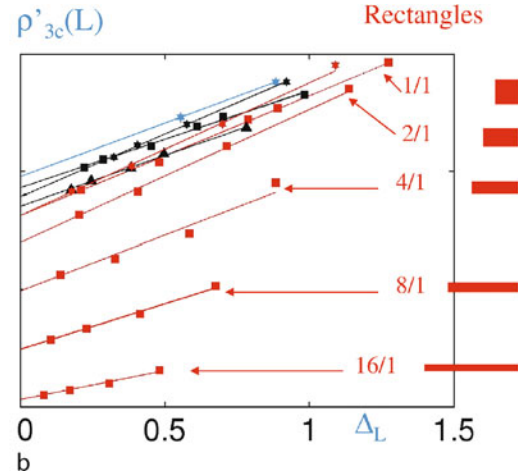
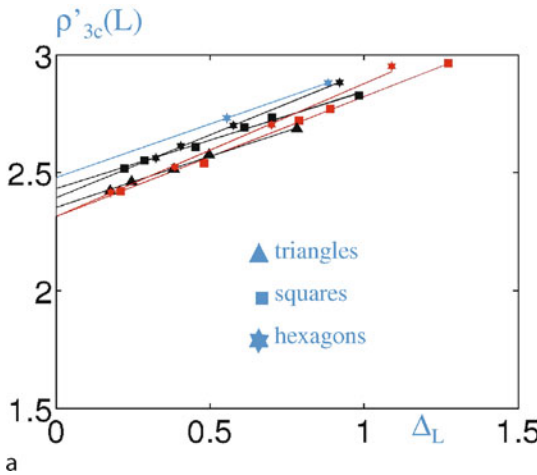
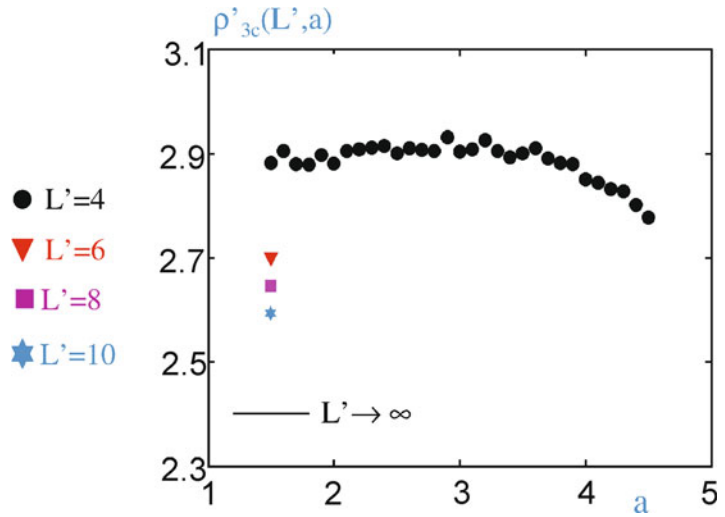
squares or triangles, or mixtures of hexagons with triangles or rectangles with a four to one aspect ratio. The upper set of curves shows that ρ'_c is indeed independent of R_m and S . Note that the rightmost points are actually monodisperse networks. For comparison, the thresholds $\rho_c \langle R^3 \rangle$, which do not include the shape factor $\langle V_{\text{ex}} \rangle$ (see Eq. 29), are also shown in the same figure and they are clearly much more scattered. It is the incorporation of $\langle V_{\text{ex}} \rangle$ in the definition of ρ'_3 which unifies the results for the different shapes

Conversely, the fracture shape (hexagonal) and the range of size ($R'_m = 0.1$) are kept constant in the example of Fig. 5, whereas the exponent a and the domain size L are varied. It is seen that ρ'_c does not vary when a ranges from 1.5 to 4. However, a definite dependence on the domain size is observed, which corresponds to the well known finite size effects.

The data for increasing L' can be extrapolated for infinite systems by use of a classical technique. The combination of (23) and (24) shows that $\rho'_c(L) - \rho'_c(\infty)$ is proportional to the width Δ_L of the percolation transition zone. Hence, $\rho'_c(\infty)$ can be read on the vertical axis of the plot of $\rho'_c(L)$

Percolation, Faults and Fractures in Rock,

Fig. 5 The percolation threshold $\rho'_{3c}(L', a)$ for networks of hexagonal fractures with $R'_m = 0.1$, versus the exponent a , for various domain sizes L' . The lower line is the extrapolation of the data for $a = 1.5$ when L' tends to infinity



Percolation, Faults and Fractures in Rock, Fig. 6 The percolation threshold $\rho'_{3c}(L')$ for mono- or polydisperse networks of fractures with various shapes, versus the width Δ_L of the percolation transition. In (a), the fractures are

hexagons, squares or triangles. $\rho'_{3c}(\infty)$ is the extrapolation for $\Delta_L \rightarrow 0$, which falls in the range of Eq. 31. Data for monodisperse networks of rectangles with aspect ratios from 1 to 16 are added in (b)

versus Δ_L , which is shown in Fig. 6. The data for many cases, including various fracture shapes in monodisperse and polydisperse networks, are gathered in Fig. 6a. In all cases, the extrapolated values $\rho'_{3c}(\infty)$ fall in the narrow range

$$\rho'_{3c}(R'_m, a, S, L' \rightarrow \infty) = \rho'_{3c}(\infty) \approx 2.4 \pm 0.1. \quad (31)$$

This applies for a variety of shapes, as well as for mixtures of fractures with different shapes (see Fig. 4).

However, when the polygons become elongated, $\rho'_{3c}(L')$ varies with the aspect ratio. Data for rectangles with aspect ratios A_r up to 16 are shown in Fig. 6b. It appears that $\rho'_{3c}(L')$ decreases significantly when A_r increases.

This can be taken into account by using the shape factor $\eta = 4R/P$ of the fractures. This ratio is minimum for disks, with $\eta = 2/\pi \approx 0.637$, and it increases up to one when the shape deviates from circularity. It turns out that a quadratic correction in terms of η is very successful for the

representation of the data for very different and irregular fracture shapes.

All the thresholds obtained in cells with $L' = 6$ and mono- or polydisperse size distributions with $a = 1.5$ or 2 and $R_m = 0.1$ are plotted in Fig. 7 as functions of η . This includes networks of hexagons, squares, triangles, mixtures of hexagons with rectangles or triangles, and rectangles with h/w up to 16 . The data are well fitted by the expression

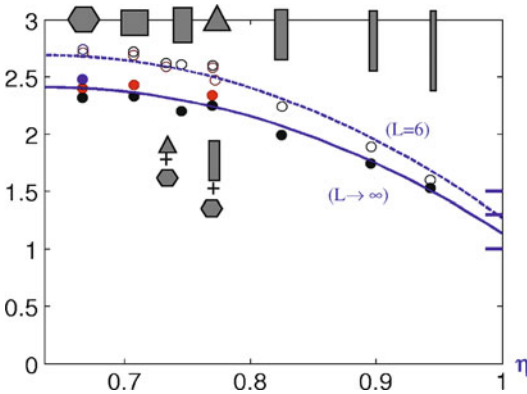
$$\rho'_{3c}(L') = 2.69 \left[1 - 4 \left(\eta - \frac{2}{\pi} \right)^2 \right] \quad (L' = 6). \quad (32)$$

The extrapolated data for infinite systems are also presented in Fig. 7, in comparison with the corrected version of Eq. (31),

$$\rho'_{3c}(\infty) = 2.41 \left[1 - 4 \left(\eta - \frac{2}{\pi} \right)^2 \right]. \quad (33)$$

In both cases, the deviations never exceed ± 0.1 . The corrective term becomes significant, i.e., larger than the error bar in (31), when $\eta > 3/4$, which corresponds for rectangles to aspect ratios larger than 2 .

It can be noted that Eq. (33) predicts a threshold value 1.14 when h/w tends to infinity (i.e., when η



Percolation, Faults and Fractures in Rock, Fig. 7 The percolation thresholds $\rho'_{3c}(L' = 6)$ and $\rho'_{3c}(\infty)$ for a variety of fracture shapes and size distributions, in comparison with the expressions (32), (33). The marks on the right are the predictions of (Florian and Neda 2001; Garboczi et al. 1995; Saar and Manga 2002) for infinitely elongated objects. The fracture shapes are indicated by the icons above or below the data points

$\rightarrow 1$), which is in the range of the predictions 1.5 for prolate ellipsoids (Garboczi et al. 1995), 1 for capped cylinders (Florian and Neda 2001) and 1.3 for elongated prisms (Saar and Manga 2002), in the limit of infinite slenderness.

Determination of the Dimensionless Density from Experimental Data

Since percolation properties are controlled by the dimensionless density ρ' , it is theoretically and practically important to derive estimations of ρ' from field data. In most cases, these data are based on 1D and 2D measurements of fracture traces along boreholes or on exposed outcrops which necessitate extrapolation by stereological techniques to 3D. Such extrapolations have already been made for specific fracture shapes by Warburton (1980a, b), Piggott (1997), Berkowitz and Adler (1998) and Sisavath et al. (2004) (see also the references therein).

Our general methodology which is detailed in Thovert and Adler (2005) can be illustrated by the intersection of a family of convex fractures with a line of length L which is parallel to the unit vector $\mathbf{p}$. Consider a fracture of surface A , of normal $\mathbf{n}$ and of in-plane orientation ω ; this object does not intersect the line when its center is located out of a surface of area A . Since this is valid for any in-plane orientation, the excluded volume of the line and of the surface is equal to $AL|\mathbf{p} \cdot \mathbf{n}|$. Hence, the average number of intersections $\langle n_I \rangle$ per unit length between such a line and an isotropic network of a monodisperse family of fractures is

$$\langle n_I \rangle = \frac{1}{2} A \rho. \quad (34)$$

Of course, the major interests of this formula are that it does not depend on the precise shape S of the fractures and that ρ can be deduced from n_I and A . However, it depends in a crucial way on the convexity of the fractures.

Isotropic Networks

In order to derive the average number of intersections Σ_I of a family of convex fractures $\mathcal{F}(R)$ with

a plane Π per unit area of the plane, define in Π a large convex region $\mathcal{R}$ of area $\mathcal{A}$ and perimeter $\mathcal{P}$. The excluded volume of $\mathcal{F}(R)$ and $\mathcal{R}$ is thus given by (8). The number of intersections $d\Sigma_t$ of the fractures of size ranging from R to $R + dR$ is proportional to the volumetric density of such fractures multiplied by the excluded volume of $\mathcal{F}(R)$ and $\mathcal{R}$ as expressed by (8); when $\mathcal{A} \rightarrow \infty$, $\mathcal{A} \gg \mathcal{P}$; therefore,

$$d\Sigma_t(R) \rightarrow \frac{1}{4} \rho P(R) n(R) dR \quad \text{when } \mathcal{A} \rightarrow \infty. \quad (35)$$

This relation can be averaged over the sizes R

$$\Sigma_t = \int d\Sigma_t(R) = \frac{1}{4} \rho \langle P \rangle. \quad (36)$$

The intersections of the fractures with a plane are called *traces* or *chords*. Let c be the length of a trace as illustrated in Fig. 1c. Such an intersection of length $c(z, \mathbf{n}, \omega)$ exists if the vertical coordinate z of the center verifies

$$z_m(\mathbf{n}, \omega) \leq z \leq z_M(\mathbf{n}, \omega). \quad (37)$$

For a given fracture of size R , the average trace length $\langle c \rangle_R$ when the intersection exists, can be expressed as

$$\langle c \rangle_R = \frac{\int d\omega \int d\mathbf{n} \int_{z_m}^{z_M} c dz}{\int d\omega \int d\mathbf{n} \int_{z_m}^{z_M} dz}. \quad (38)$$

Surprisingly, the numerator N_R of this fraction is easier to evaluate than its denominator D_R . The most internal integral $\int_{z_m}^{z_M} c dz$ is equal to the area A of the fracture projected onto the plane perpendicular to Π which contains the trace, i.e., $A \sin \theta$. Therefore, N_R is equal to $\pi^3 A$. The derivation of D_R is slightly more involved Santalo (1943); it is proportional to the integral of the Feret (or caliper) diameter over ω . Frenet formulae are used to express this integral. Finally,

$$\langle c \rangle_R = \pi \frac{A(R)}{P(R)}. \quad (39)$$

For polydisperse fractures, the overall average $\langle c \rangle$ is given by

$$\langle c \rangle = \frac{\int dR \Sigma_t(R) \langle c \rangle_R}{\int dR \Sigma_t(R)} = \pi \frac{\langle A \rangle}{\langle P \rangle} \quad (40)$$

a formula which is again an obvious generalization of the disk formula (cf. (24a) of Berkowitz and Adler (1998)).

The density of trace intersections Σ_p is defined as the number per unit surface in the observation plane of the points which are intersections of traces. Since the fractures are randomly oriented and distributed in space, the same properties are valid for the traces. Moreover, as a trivial extension of the concept of excluded volume, the excluded surface S_{ex} of two traces of random orientations and of lengths c_1 and c_2 is equal to (cf. Adler and Thovert 1999)

$$S_{\text{ex}} = \frac{2}{\pi} c_1 c_2. \quad (41)$$

Let $\sigma_t(R, c) dc dR$ be the surface density of traces of length c ranging from c to $c + dc$, for the fractures of size R ranging from R to $R + dR$. Hence, the surface density of intersections of traces c_1 corresponding to fractures of size R_1 and of traces c_2 corresponding to fractures of size R_2 is

$$\sigma = \frac{1}{2} \sigma_t(R_1, c_1) \sigma_t(R_2, c_2) \frac{2}{\pi} c_1 c_2. \quad (42)$$

As a direct consequence

$$\Sigma_p = \int \int \int \int \sigma dc_1 dR_1 dc_2 dR_2. \quad (43)$$

This last expression can be split into a product of integrals since the populations 1 and 2 are independent. According to (35), (36), (43), Σ_p can be expressed as

$$\Sigma_p = \frac{1}{\pi} \frac{\pi^2}{16} \rho^2 \langle A \rangle^2 = \frac{\pi}{16} \rho^2 \langle A \rangle^2. \quad (44)$$

Extensions

Let us now examine various possible extensions of the previous formulae.

The precise shape S of the fractures is never taken into account. Therefore, all the previous formulae are valid whatever the mixture of shapes S .

For anisotropic networks, the normal vector $\mathbf{n}$ is not uniformly distributed over the unit sphere. Let θ and φ be the two polar angles of $\mathbf{n}$ (cf. Fig. 1c); the probability that the end of $\mathbf{n}$ for fractures of sizes in the interval $[R, R + dR]$ belongs to the interval $[\theta, \theta + d\theta] \times [\phi, \phi + d\phi]$ is given by $\rho n(R, \mathbf{n}) d\theta d\phi dR$. The statistical average $\langle \cdot \rangle$ can be calculated with this differential element.

The first quantity which can be easily generalized is $\langle n_I \rangle$ (cf. (34))

$$\begin{aligned} \langle n_I \rangle &= \rho \int \int \int n(R, \mathbf{n}) A \cos \theta \, d\theta \, d\phi \, dR \\ &= \rho \langle A |\mathbf{p} \cdot \mathbf{n}| \rangle. \end{aligned} \quad (45)$$

The other generalized formulae are summarized in Table 2. α is the angle between the normal $\mathbf{v}$ to the plane Π and $\mathbf{n}$; in most cases, by choosing the z -axis perpendicular to Π , α is equal to θ ; β_{12} is the angle between the normals $\mathbf{n}_1$ and $\mathbf{n}_2$ to the two fractures 1 and 2.

These formulae can be specialized to networks of sub-vertical fractures with a horizontal observation plane Π . Then, α is equal to $\pi/2$ and β_{12} is equal to the angles between the two traces in Π . Such networks can be either isotropic (i.e., the directions of the traces in Π are isotropic), or

anisotropic. The corresponding results are detailed in Table 2.

Discussion

Discrete Families of Fractures In many practical cases, the fractures are perpendicular to a finite set of normals $\{\mathbf{n}_i; i = 1, \dots, m\}$ with probabilities $\{n(R, \mathbf{n}_i); i = 1, \dots, m\}$. The integrals over $d\theta d\phi$ are thus replaced by the following summation for a function $f(R, \mathbf{n}_i)$

$$\rho \sum_{i=1}^m n(R, \mathbf{n}_i) f(R, \mathbf{n}_i). \quad (46)$$

Practical Use of the Formulae The major interest of the formulae summarized in Table 2 is to try to use them to derive the macroscopic quantities ρ , $\langle A \rangle$ and $\langle P \rangle$. It is easy (and frustrating) to realize that only two of these quantities can be obtained. For instance, (40) implies that $\langle A \rangle = \pi^{-1} \langle P \rangle \langle c \rangle$; from (36), $\langle P \rangle = 4\rho^{-1} \Sigma_t$; therefore $\langle A \rangle = 4\pi^{-1} \rho^{-1} \Sigma_t \langle c \rangle$. When these expressions are introduced into (34) or (44), one obtains that the following three ratios should be equal to one

$$\begin{aligned} \kappa_1 &= \frac{\pi}{2} \frac{\langle n_I \rangle}{\Sigma_t \langle c \rangle}, & \kappa_2 &= \frac{\pi \Sigma_p}{\Sigma_t^2 \langle c \rangle^2}, \\ \kappa_3 &= \frac{\pi}{4} \frac{\langle n_I \rangle^2}{\Sigma_p}. \end{aligned} \quad (47)$$

The third relation is derived by eliminating $\Sigma_t \langle c \rangle$ between κ_1 and κ_2 . These relations provide consistency relations between the data, but not ρ .

In other words, only two of the three quantities ρ , $\langle A \rangle$ and $\langle P \rangle$ can be simultaneously derived

Percolation, Faults and Fractures in Rock, Table 2 The major relations for the various kinds of networks. $\mathcal{B}_{12} = \langle A_1 A_2 |\sin \beta_{12}| \rangle$

	Isotropic 3D	Anisotropic 3D	Subvertical isotropic	Subvertical anisotropic
$\langle n_I \rangle$	$\frac{1}{2} \rho \langle A \rangle$	$\rho \langle A \mathbf{p} \cdot \mathbf{n} \rangle$	$\frac{2}{\pi} \rho \langle A \rangle$	$\rho \langle A \mathbf{p} \cdot \mathbf{n} \rangle$
Σ_t	$\frac{1}{4} \rho \langle P \rangle$	$\frac{\rho}{\pi} \langle \sin \alpha P \rangle$	$\frac{\rho}{\pi} \langle P \rangle$	$\frac{\rho}{\pi} \langle P \rangle$
$\langle c \rangle$	$\pi \frac{\langle A \rangle}{\langle P \rangle}$	$\pi \frac{\langle A \sin \alpha \rangle}{\langle P \sin \alpha \rangle}$	$\pi \frac{\langle A \rangle}{\langle P \rangle}$	$\pi \frac{\langle A \rangle}{\langle P \rangle}$
Σ_p	$\frac{\pi}{16} \rho^2 \langle A \rangle^2$	$\frac{1}{2} \rho^2 \mathcal{A}_{12}$	$\frac{1}{\pi} \rho^2 \langle A \rangle^2$	$\frac{\rho^2}{2} \mathcal{B}_{12}$

from the average measured data. Note also that κ_1 is insensitive to the spatial organization, and that this is not true for κ_2 and κ_3 which depend on trace intersections.

One can go further if some geometrical information is available which could be $\langle V_{\text{ex}} \rangle$. Here, we shall use a shape factor η which is defined as $\langle A \rangle \langle P \rangle^{-2}$. For 3D isotropic networks, this expression can be combined to (40) and to (36) to yield $\langle A \rangle$, $\langle P \rangle$ and ρ

$$\langle P \rangle = \frac{\langle c \rangle}{\pi \eta}, \quad \langle A \rangle = \frac{\langle c \rangle^2}{\pi^2 \eta}, \quad \rho = 4\pi \eta \frac{\Sigma_t}{\langle c \rangle} \quad (48)$$

or for a set of fractures normal to $\mathbf{n}_i$

$$\rho_i = \frac{\pi^2 \eta_i}{|\sin \alpha_i|} \frac{\Sigma_{ti}}{\langle c \rangle_i}. \quad (49)$$

There are many equivalent ways to derive ρ . The choice of the adequate formula depends on the available data. Note that formulae which contains Σ_p cannot be applied to families of parallel fractures.

When ρ and therefore $\langle V_{\text{ex}} \rangle$ (cf. (8)) are known by one way or another, one can derive the dimensionless density $\rho' = \rho \langle V_{\text{ex}} \rangle$ for isotropic and anisotropic networks

$$\rho' = \frac{\rho}{\pi} \langle (A_1 P_2 + A_2 P_1) |\sin \beta_{12}| \rangle \quad (50)$$

$$\begin{aligned} \rho' &= \frac{\rho}{2} \langle A \rangle \langle P \rangle \quad (3d); \\ \rho' &= \frac{4\rho}{\pi^2} \langle A \rangle \langle P \rangle \quad (2d). \end{aligned} \quad (51)$$

Then, if the fracture network is not too polydisperse, one can use a classical mean field argument and approximate its properties by the properties of a monodisperse network of density ρ' .

Applications

Several applications have already been made of the previous methodology and they can be summarized as follows. Sisavath et al. (2004) showed that when data relative to fractures are collected

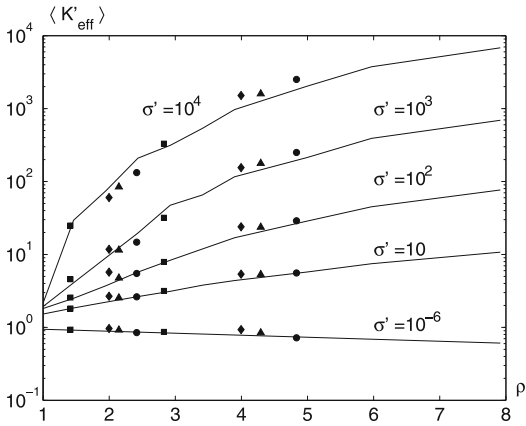
along a line (e.g. a road or a well), estimations can be given to the major geometrical properties of the corresponding fracture networks, such as the volumetric density of fractures and their percolation character. Thovert and Adler (2005) used the two dimensional maps obtained by Odling (1997) for subvertical fractures. Among other results, some of the consistency relationships (47) are well verified by these data. As previously, ρ' is estimated.

Finally Gonzalez Garcia et al. (2000), reconstructed a three-dimensional fracture network in a granite block from a series of experimental serial sections provided by Ledésert et al. (1993). It was visualized and its most important geometrical characteristics were studied. Though the network mostly consists of two families of fractures, it is interesting to note that a simple model of randomly oriented, monodisperse hexagons often yields a good order of magnitude for the various geometrical properties, which have been measured on the real block.

Role of the Dimensionless Density in Other Geometrical Properties and Permeability

Though this chapter is focused on percolation properties, it is important to notice that the dimensionless densities which were introduced, play a crucial role in other properties as well. Huseby et al. (1997) studied two main other geometrical properties for monodisperse networks. Fracture networks partition the solid space into blocks; the block density is denoted by ρ_b . One can introduce the cyclomatic number of the graph Γ_1 which is the number of independent cycles of this graph, and more precisely the number of cycles $\bar{\beta}_1$ per unit volume. Huseby et al. (1997) showed that ρ_b and $\bar{\beta}_1$ when made dimensionless by the excluded volume are independent of the fracture shapes.

Similar properties are found for the macroscopic permeability of fracture networks (Koudina et al. 1998) and of fractured porous media whether they are monodisperse (Bogdanov et al. 2003) or polydisperse (Mourzenko et al. 2004a). In a series of contributions, the corresponding dimensionless quantities were



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Fig. 8 Statistical averages of the permeability $\langle K'_{\text{eff}} \rangle$ for samples containing $N_f = 16$ or 32 fractures, with 4-, 6- or 20-gonal shapes, as functions of the network density ρ' and of the fracture conductivity σ' . The cell size is $L = 4R$. Data are for squares ($\square$), rectangles with aspect ratios two to one (Δ) or four to one ($\diamond$), hexagons (lines) and icosagons (o)

shown to depend only on the dimensionless density ρ' . This is illustrated in Fig. 8. The porous medium has a local permeability K_m and the monodisperse fractures a conductivity σ . The macroscopic permeability of this medium is denoted by K_{eff} . Dimensionless quantities denoted by primes can be defined as

$$\sigma = R K_m \sigma', \quad K_{\text{eff}} = K_m K'_{\text{eff}}. \quad (52)$$

Figure 8 shows that the average macroscopic permeability $\langle K'_{\text{eff}} \rangle$ does not depend significantly on the fracture shape. The two major parameters are ρ' and σ' .

Future Directions

The percolation properties of networks of random and convex plane fractures are successfully addressed by means of the excluded volume. Many important dimensionless properties of isotropic fracture networks only depend on the dimensionless density of fractures and not on the fracture shapes and sizes which represents a significant simplification.

These properties are not specific of fractures present in rocks and the same methodology can be applied for any other fracture system whatever the characteristic sizes and the nature of the material where it occurs.

These results should be generalized in several directions. In most cases, real fractures are not isotropically oriented and this feature should be incorporated in the next studies on this subject. The same is true for the homogeneous character of the network.

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Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis

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Article Outline

Introduction
Conductance of a Pore
Estimating Permeability by CPA
Applications to Tight-Gas Sandstones
Applications to Soils
Applications to Packings of Grains
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Introduction

Accurate estimation of permeability k in rocks and soils is still of great interest in hydrology, soil physics, petroleum engineering, and geoscience. It has broad applications in investigating fluid flow and solute transport in aquifers, as well as determining hydrocarbon production from geological formations. By definition, permeability is a measure representing the complex relationship between the geometry and topology of the pore space and flow of a fluid through it. In rigid porous media, the permeability is independent of the type of the fluid. However, some fluids may interact with the solid matrix and alter the medium permeability. Swelling of clay minerals and blockage of pore space by trapped gas may, for example, cause discrepancy between gas and liquid permeability in rocks. In addition to solid-fluid interactions that may alter the solid's structure, gas permeability may not necessarily match liquid permeability

because of gas slippage at the pore-solid interface (Klinkenberg 1941), as well as its compressibility.

The literature on estimating permeability based on other properties of porous media is extensive. Numerous empirical, semi-physical and theoretical models have been proposed based on various methods to estimate permeability from porosity and grain-size distribution (Kozeny 1927; Carman 1937; Panda and Lake 1994; Porter et al. 2013; Koltermann and Gorelick 1995), mercury intrusion porosimetry (Swanson 1981; Thomeer 1960; Katz and Thompson 1986; Ghanbarian et al. 2016a, 2019), formation factor (Johnson et al. 1986; Revil and Cathles 1999; Weller et al. 2015; Freund and Nover 1995), and nuclear magnetic resonance (Timur 1968; Coates et al. 1999; Glover et al. 2006). Among the proposed techniques, upscaling approaches from statistical physics, such as percolation theory (Stauffer and Aharony 1994; Sahimi 1994; Heiba et al. 1992; Larson et al. 1981), critical-path analysis (Hunt 2001; Ambegaokar et al. 1971; Pollak 1972), effective-medium approximation (Shante and Kirkpatrick 1971; Kirkpatrick 1973; Sahimi 2003; Richesson and Sahimi 2019; Sahimi et al. 1984), renormalization group theory (Bernasconi 1978; King 1989; Fisher 1998), real-space renormalization and effective-medium approximation (Sahimi et al. 1983), and percolation-based effective-medium approximation (Deprez and McLachlan 1988; McLachlan and Sauti 2007; Ghanbarian and Daigle 2016a; Sadeghi et al. 2018) have been successfully applied to model flow and transport in porous media. For a recent review, see Hunt and Sahimi (2017).

In this chapter, we focus on one theoretical approach to estimating the effective permeability, namely, the critical-path analysis (CPA). We describe the basic concepts based on which the CPA was developed, and discuss its applications to various types of porous media, such as unconventional reservoirs, soils, and packing of grains.

Conductance of a Pore

To scale up permeability and electrical conductivity in a porous medium from pore to core, it is necessary to assume specific pore shape and geometrical characteristics. Two common assumptions in the literature are cylindrical and slit-shaped pores (Rijfkogel et al. 2019). The hydraulic (g_h) and electrical (g_e) conductances of a cylindrical pore of diameter d and length l filled with a fluid of viscosity μ and electrical conductivity of σ_w are, respectively (Banavar and Johnson 1987).

$$g_h = \frac{\pi d^4}{128 \mu l} \propto d^{\gamma_h} \quad (1)$$

and,

$$g_e = \frac{\pi \sigma_w d^2}{4l} \propto d^{\gamma_e} \quad (2)$$

where $\gamma_h = 4$ and $\gamma_e = 2$, if d and l are independent. If the pores have self-similar structure, one may assume $d \propto l$ and, thus, $\gamma_h = 3$ and $\gamma_e = 1$ (Katz and Thompson 1986).

For slit-shaped pores of width w much narrower than its breadth b and length l , Eqs. (1) and (2) change to (Friedman and Seaton 1998).

$$g_h = \frac{bw^3}{12 \mu l} \propto w^{\gamma_h} \quad (3)$$

and,

$$g_e = \frac{\sigma_w bw}{l} \propto w^{\gamma_e} \quad (4)$$

Similarly, $\gamma_h = 3$ and $\gamma_e = 1$, if w is independent of l , and $\gamma_h = 2$ and $\gamma_e = 0$, if $w \propto l$.

Estimating Permeability by CPA

Among theoretical approaches developed to predict permeability, such as bundle of capillary tubes (Purcell 1949; Childs and Collisgeorge 1950; Yu and Cheng 2002; Marshall 1958; Wei

et al. 2018) and effective-medium approximations (Doyen 1988; David et al. 1990; Ghanbarian and Daigle 2016b), the critical-path analysis (CPA), which is based on percolation theory (Ambegaokar et al. 1971; Pollak 1972), appears to be an accurate method, particularly in heterogeneous porous media (Hunt 2001; Hunt and Gee 2002; Arns et al. 2005; Hunt et al. 2014). Ambegaokar et al. (1971) argued that fluid flow or transport in disordered media with a broad conductance distribution is dominated by those with magnitudes that are larger than some critical conductance, g_c , which is the smallest conductance among the set of conductances, $g \geq g_c$, forming a sample-spanning cluster. In other words, g_c is the smallest conductance along the path of least resistance through the medium. According to CPA, pores with a small conductance and finite volume fractions make a negligible contribution to the overall permeability. Therefore, such zones of low permeability may be eliminated from the medium, which would then reduce it to a percolation system (Hunt et al. 2014; Sahimi 2011).

Katz and Thompson (1986, 1987) were the first to apply the CPA to relate the permeability to electrical conductivity and critical pore diameter in rocks. They assumed that in a porous medium, the diameter d of a cylindrical pore is linearly proportional to its length l ($d \propto l$) and expressed the hydraulic g_h and electrical g_e conductances as $g_h \propto d^{\gamma_h}$ and $g_e \propto d^{\gamma_e}$ in which $\gamma_h = 3$ and $\gamma_e = 1$. Analogously, as pointed out earlier, one should expect $\gamma_h = 4$ and $\gamma_e = 2$, if d and l are independent, e.g., fixed pore length in a pore-network model.

The Katz and Thompson (1986) model is:

$$k = \frac{1}{c} \frac{\sigma_b}{\sigma_w} d_c^2 = \frac{d_c^2}{cF} \quad (5)$$

where σ_b is the bulk electrical conductivity, σ_w is the electrical conductivity of the saturating fluid, $F = \sigma_w/\sigma_b$ is the formation factor, d_c is critical pore diameter, and c is a constant equal to 226 (hereafter, c_{KT}). Following Chatzis and Dullien (1977) and de Gennes and Guyon

(1978), Katz and Thompson (1986, 1987) argued that the inflection point on the mercury intrusion porosimetry curve corresponds to the critical pore diameter and the saturation at which a sample-spanning cluster first forms. In addition to the mercury intrusion porosimetry, estimating permeability using Eq. (5) requires the electrical conductivity, which may be estimated from mercury intrusion (Katz and Thompson 1987) or water-expulsion (Nishiyama and Yokoyama 2014) porosimetry, if not measured.

Equation (5) is similar in form to what Johnson et al. (1986) proposed for estimating the permeability, i.e., $k = \Lambda^2/8F$ in which Λ is a characteristic pore length, a measure of dynamically connected pore sizes. Martys and Garboczi (1992) showed that both Λ and d_c are good predictors of the permeability in two-dimensional pore-network models. In particular, Martys and Garboczi (1992) stated that, “In a random pore structure, with a distribution of pore sizes, the flow will tend to go more through the largest pore necks, decreasing the importance of the narrowest necks that tend to dominate the behavior of periodic models.” Although Bernabé and Bruderer (1998) documented results similar to those of Martys and Garboczi (1992) in two dimensions, they found that flow pathways in porous media with broadly distributed pore sizes were not restricted to the backbone or the critical paths. For permeability modeling using the CPA in highly heterogeneous media, see also Shah and Yortsos (1996).

Arns et al. (2005) evaluated the relationships that are used to estimate permeability from the properties of the pore-size distribution in Fontainebleau sandstones, based on three-dimensional digitized images. They considered relationships that were based on the ratio of pore volume to surface area, critical pore diameter (associated with mercury intrusion porosimetry data), characteristic pore sizes associated with nuclear magnetic resonance relaxation time T_2 , as well as the mean survival time of a probe molecule in a pore space before it reacts. They found that all the relationships that they evaluated provided good agreement with their lattice-Boltzmann simulations. However, estimated of

the permeability based on the critical pore diameter, i.e., the CPA, were most reliable.

Banavar and Johnson (1987) revisited the Katz and Thompson (1986) model and found the constant coefficient in Eq. (5) $c_{BJ} = 130.2$, different from $c_{KT} = 226$ obtained by Katz and Thompson (1986). Although Banavar and Johnson (1987) maximized the corresponding effective transport coefficient and assumed that the electrical conductivity and/or permeability was proportional to that maximum value, Katz and Thompson (1986) divided that maximum value by the corresponding maximizing pore size. For further details and discussions, see Banavar and Johnson (1987).

Following the results of Tyč and Halperin (1989) on random resistor networks with broadly distributed conductances, Le Doussal (1989), and more recently Skaggs (2011), proposed the relationship

$$k = \frac{1}{32} \left[\frac{\gamma_h}{\gamma_e} \right]^{-y} \frac{\sigma_b}{\sigma_w} d_c^{\gamma_h - \gamma_e} = \frac{1}{c} \frac{\sigma_b}{\sigma_w} d_c^2 \quad (6)$$

Le Doussal (1989) argued that the prefactor exponent $y = v = 0.88$, where v is the universal exponent that characterizes the power-law divergence of the correlation length near the percolation threshold in three dimensions. However, subsequent numerical simulations and evaluation of the of critical path of the conductivity on random resistor networks indicated that $y < v$. Skaggs (2003) showed that the observed $y < v$ is due to the effects of finite heterogeneity, not finite size, and found $y = 0.74 \pm 0.01$ by means of Monte Carlo simulations.

The values of the constant coefficients in the theories proposed by Le Doussal (1989) and the Skaggs (2011) (hereafter referred to as c_L and c_S), the numerical prefactor corresponding respectively to $y = 0.88$ and 0.74 in Eq. (6) under different circumstances are given in Table 1. As can be observed, depending on the relationship between the pore diameter d and its length l , the c_L differs from c_{KT} by a factor of 3 or 4. Other values of c proposed by Banavar and Johnson (1987) and Friedman and Seaton (1998) are also listed in Table 1.

Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Table 1 Values of constant c in Eqs. (5) and (6) reported in the literature

Reference	γ	γ_h	γ_e	$1/c$	c^a
Katz and Thompson (1986)	—	3	1	4.42×10^{-3}	226
Banavar and Johnson (1987)	—	3	1	7.68×10^{-3}	130.2
Le Doussal (1989)	0.88	3	1	1.19×10^{-2}	84.1
	0.88	4	2	1.70×10^{-2}	58.9
	0.88	3.5	1.5	1.48×10^{-2}	67.5
Skaggs (2011)	0.74	3	1	1.39×10^{-2}	72.2
	0.74	4	2	1.87×10^{-2}	53.5
Friedman and Seaton (1998)	—	—	—	3.13×10^{-2}	32

^a c represents a constant coefficient in each model, e.g., c_{KT} is the Katz and Thompson, c_{BJ} is the Banavar and Johnson, c_L is the Le Doussal, c_S denotes the Skaggs, and c_{FS} is the Friedman and Seaton numerical prefactor in the context

Applications to Tight-Gas Sandstones

Tight and ultra-tight reservoirs have been successfully explored, and have produced, not only in the United States and North America, but also in China. Accordingly, they have become a major contributor to energy supplies. Although research on fluid flow in tight-gas sandstones and shales has made significant progress over the past decade (Ghanbarian et al. 2016a; Javadpour 2009; Civan et al. 2011; Ghanbarian and Javadpour 2017; Tahmasebi et al. 2015, 2016; Ghanbarian et al. 2020), there is still a long way to fully understand the mechanisms and key factors that control oil and gas transport in such formations.

To experimentally evaluate the CPA for estimating permeability in unconventional reservoir rocks, Ghanbarian et al. (2016a) selected 18 tight-gas sandstones. Samples were cut from whole cores retrieved in a tight-gas sandstone formation located in East Texas. Table 2 summarizes the salient properties of each rock sample. In all samples, permeability was measured by gas flow and corrected for the Klinkenberg effect. Mercury intrusion porosimetry was used to determine the pore-throat size distribution of each sample. The critical pore diameter was determined from the inflection point on the mercury intrusion porosimetry curve. The cumulative pore volume V and the difference in pore volume ΔV as a function of the pore diameter d are shown for one sample in Fig. 1.

Bulk electrical conductivity σ_b was measured under fully saturated conditions. The measured electrical conductivity σ_w of the saturating fluid was then used to normalize the electrical conductivity and determine the formation factor $F = \sigma_w/\sigma_b$. From the measured electrical conductivity-saturation curve (not shown), it was found that the effect of surface conduction was negligible in these rocks.

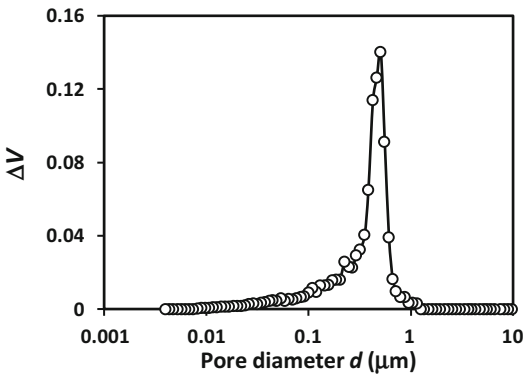
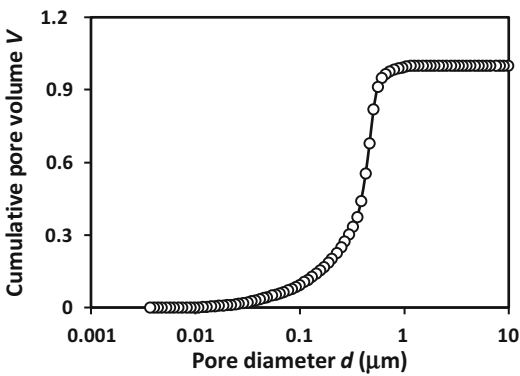
Figure 2 shows the measured permeability k as a function of the calculated critical pore diameter for 18 rock samples. If samples 16 and 18 are excluded, k is relatively highly correlated to d_c ($R^2 = 0.72$). Although there are scatters, the exponent 2.13 of the power law fit to the experimental data is not greatly different from the theoretical value of 2; see Eqs. (5) and (6). Katz and Thompson (1987) stated that the largest error in the calculation of the critical pore diameter may be due to injection rates that are too high.

Figure 3 compares the permeability estimates using the Katz and Thompson (1986), Le Doussal (1989), and Skaggs (2011) CPA and theories with the measurements. As shown in the figure, the Katz-Thompson (1986) CPA model substantially underestimates k , although Katz and Thompson (1986) emphasized that their model estimates well the permeability of sandstones and a few carbonates. Comparison of the RMSLE values indicates that the Katz-Thompson model is the least accurate among those studied by Ghanbarian et al. (2016a). The results are consistent with those of Kamath et al. (1992) who estimated the permeability from measured mercury intrusion

Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Table 2 Selected properties of the 18 tight-gas sandstone samples used within the study of Ghanbarian et al. (2016a)

Sample	Porosity ϕ	Formation factor $F = \sigma_w/\sigma_b$	Gas permeability k (μm^2)	Critical pore diameter d_c (μm)
1	0.068	343.6	1.09×10^{-5}	0.39
2	0.074	319.0	1.38×10^{-5}	0.47
3	0.086	258.7	2.96×10^{-5}	0.60
4	0.072	254.7	2.47×10^{-5}	0.32
5	0.089	224.3	3.95×10^{-5}	0.73
6	0.079	271.5	1.78×10^{-5}	0.56
7	0.069	305.6	1.78×10^{-5}	0.57
8	0.077	291.0	2.07×10^{-5}	0.61
9	0.067	402.2	6.91×10^{-6}	0.35 ^a
10	0.057	331.0	2.96×10^{-6}	0.25 ^a
11	0.083	231.6	1.28×10^{-5}	0.51
12	0.084	255.6	8.88×10^{-6}	0.39
13	0.043	809.3	1.18×10^{-6}	0.20 ^a
14	0.073	293.2	4.93×10^{-6}	0.28
15	0.073	242.5	2.57×10^{-5}	0.42
16	0.050	488.6	3.85×10^{-5}	0.13 ^a
17	0.062	294.7	8.88×10^{-6}	0.30
18	0.069	333.9	1.97×10^{-6}	0.09 ^a

^aThe critical pore diameter was determined from the inflection point by fitting the van Genuchten capillary pressure curve model to the mercury intrusion porosimetry data



Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 1 Cumulative volume V of the pores invaded by mercury (left) and the difference

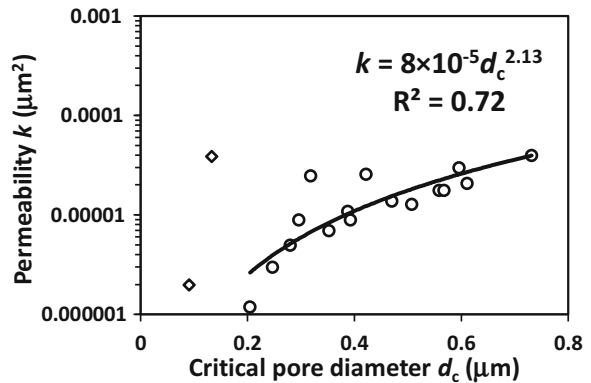
in pore volume ΔV (right) as a function of pore diameter for a tight-gas sandstone sample (Ghanbarian et al. 2016a)

porosimetry using the Katz-Thompson (1987) model, and found substantial permeability underestimation.

The results also indicate that the assumption of independence of d from l could be more realistic in tight-gas sandstones. As can be deduced from the RMSLE values reported in

Fig. 3, the Skaggs (2011) and Friedman and Seaton (1998) models estimated permeability more accurately than others. Based on the CPA, Friedman and Seaton (1998) assumed that permeability and electrical conductivity are only affected by their critical conductances and proposed a model similar to Eq. (5) with

Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 2 Measured permeability as a function of critical pore diameter for all 18 tight-gas sandstone samples. Black diamonds identify outliers (i.e., samples 16 and 18 in Table 2)



$c = 32$. Consequently, in their framework, the numerical prefactor c_{FS} is equal to 32, a value substantially less than 226 proposed by Katz and Thompson (1986, 1987), and considerably less than those reported in Table 1. The reason for such large discrepancies is that Friedman and Seaton (1998) simply related permeability to electrical conductivity through their critical conductances, i.e., $g_c^h = \pi r_c^4 / 8 \mu l$ and $g_c^e = \pi \sigma_w r_c^2 / l$ in which r_c is the critical pore radius. However, Katz and Thompson (1986, 1987) took into account the nontrivial effect of the connected path. They stated that (Katz and Thompson 1987), “The percolation model properly weights the importance of the first connected path of large pores to the total conductivity. That weighting is reflected in the value of the constant $1/226$.” The effect of such weighting factor was also considered by Banavar and Johnson (1987), Le Doussal (1989), and Skaggs (2011). Nonetheless, there exists numerical evidence in the literature (see, e.g., Bernabé (1995)) indicating that the Friedman and Seaton (1998) model, i.e., $k = d_c^2 / (32F)$, may estimate permeability accurately in two-dimensional pore-network models. Surprisingly, numerical simulations performed on digital rock models derived from various types of rocks, e.g., carbonate, sandstone, consolidated and unconsolidated, also support a constant coefficient as low as 32 (Bauget et al. 2005; Knackstedt et al. 2006).

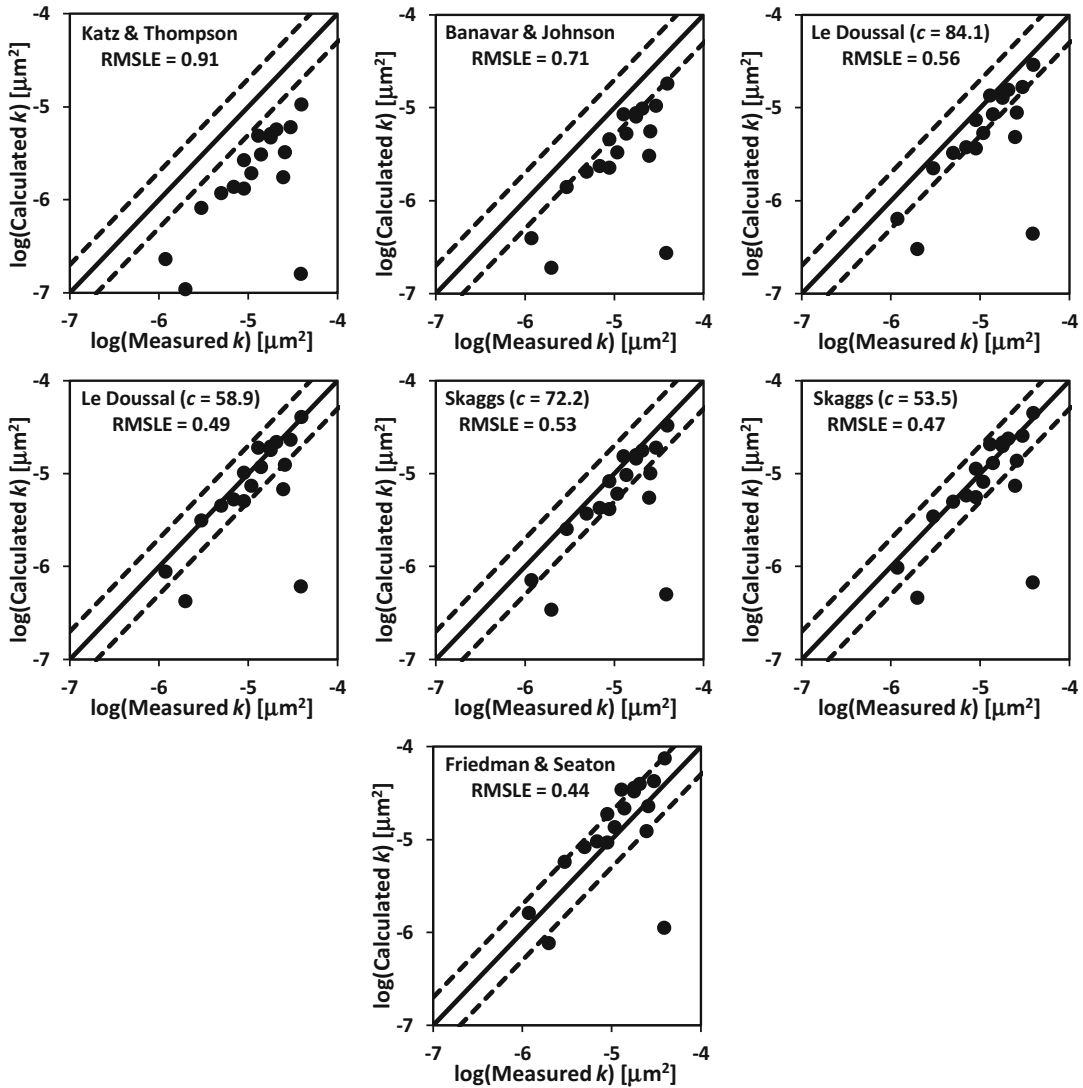
Comparison of the estimates of the Friedman and Seaton (1998) approach to experiments shown in Fig. 3 indicates that their approach overestimates the permeability remarkably in tight-gas sandstones. Although comparison of the RMSLE

values indicates that the Friedman-Seaton (1998) model estimates permeability slightly better than the Skaggs (2011) model, it should be pointed out that such results are mainly due to better k estimates for samples 18, and especially 16, whose large error contributes significantly to the RMSLE value.

Applications to Soils

Estimating saturated hydraulic conductivity K_{sat} (or permeability) from microscopic and macroscopic soil properties has been an intensive research area since the 1940s. Early pioneering models were developed based on the bundle of capillary tubes approach, idealizing a porous medium by replacing actual interconnected flow paths with straight cylindrical pore tubes of equal length (Purcell 1949; Childs and Collisgeorge 1950). For example, Marshall (1958) proposed a model similar to Purcell (1949) and Childs and Collis-George (1950) that estimated permeability k from a measured capillary pressure curve. In the Marshall (1958) model, the capillary pressure curve is classified into n sections, each of which is assumed to correspond to a fraction $1/n$ of the total pore cross-sectional area, characterized by a mean pore radius. The average cross-sectional area of the pore space is then calculated and related to permeability k .

Using concepts from the CPA, one may define the critical volume content of percolation, θ_t , under fully saturated conditions as follows (Ghanbarian-Alavijeh and Hunt 2012a):



Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 3 Logarithm plots of the estimated permeability using various models versus experimental data

$$\theta_t = \int_{r_c}^{r_{\max}} sr^3 f(r) dr = \frac{sC_p}{3-D} (r_{\max}^{3-D} - r_c^{3-D}) \quad (7)$$

where s is the shape factor, C_p is a normalization factor, $r_{\max}$ is the largest *accessible* pore throat radii representing the upper bound of the fractal scaling, r_c is the critical pore throat radius below which pores do not substantially contribute to fluid flow and permeability, and D is the fractal dimension of the pore space whose value in three

dimensions is typically between 0 and 3 in natural porous media, such as soils and rocks (Hunt et al. 2014; Ghanbarian and Millán 2017; Pachepsky et al. 2000). However, Ghanbarian-Alavijeh and Hunt (2012b) demonstrated that the theoretical range of the pore space fractal dimension is between $-\infty$ and 3, in accord with the results of Mandelbrot (1990, 1991).

Given that $\beta = \phi r_{\max}^{3-D} / (r_{\max}^{3-D} - r_{\min}^{3-D})$ (Ghanbarian-Alavijeh and Hunt 2012a), rewriting Eq. (7) yields

$$r_c = r_{\max} \left[1 - \frac{\theta_t}{\beta} \right]^{\frac{1}{3-D}} \quad (8)$$

where $r_{\max}$ can be estimated from the air entry pressure ($P_a = A/r_{\max}$). Therefore, if $r_{\max}$, θ_t , β , and D are known, one may calculate the critical pore radius r_c via Eq. (8). In Eq. (8), the greater the critical water content θ_t , the smaller is the critical pore radius r_c . When $\theta_t = 0$, the critical pore radius would be equal to the maximum accessible pore radius ($r_c = r_{\max}$).

If the value of formation factor is not measured, the electrical conductivity σ_b/σ_w can be approximated from the capillary pressure curve, as Katz and Thompson (1987) proposed

$$\frac{\sigma_b}{\sigma_w} = \frac{1}{F} = \frac{r_{\max}^e}{r_c} \phi S(r_{\max}^e) \quad (9)$$

where $r_{\max}^e$ is the pore throat radius corresponding to optimum path for electrical conductivity, $S(r_{\max}^e)$ is the fractional volume of connected pore space involving pore throats of size $r_{\max}^e$ and greater. Katz and Thompson (1987) argued that when the pore-throat size distribution is broad, $r_{\max}^e$ can be estimated from $[1 - t/(1 + t)]r_c$ in which t is a critical exponent that characterizes the power-law vanishing of the conductivity near the percolation threshold, whose value is equal to 2 in three dimensions (Stauffer and Aharony 1994; Sahimi 1994). Accordingly, $r_{\max}^e$ would be *roughly* $r_c/3$.

Analogous to Eq. (7), one may define $S(r_{\max}^e)$ as follows:

$$\begin{aligned} S(r_{\max}^e) &= \frac{1}{\phi} \int_{r_{\max}^e}^{r_{\max}} sr^3 f(r) dr \\ &= 1 - \left(\frac{r_{\max}^e}{r_{\max}} \right)^{3-D} \end{aligned} \quad (10)$$

Approximating $r_{\max}^e$ by $r_c/3$ and combining Eqs. (9) and (10) gives

$$\frac{\sigma_b}{\sigma_w} = \frac{\phi}{3} \left[1 - \left(\frac{r_c}{3r_{\max}} \right)^{3-D} \right] \quad (11)$$

Equation (11) estimates the electrical conductivity σ_b/σ_w from pore throat characteristics $r_{\max}$, r_c , and D , as well as porosity ϕ .

Ghanbarian et al. (2017) substituted the critical pore radius r_c and electrical conductivity σ_b/σ_w from Eqs. (8) and (11) into the Katz and Thompson (1986) model and derived the following equation for the saturated hydraulic conductivity

$$K_{\text{sat}} = f_f \frac{A^2 P_a^{-2}}{C_{KT}} \frac{\phi}{3} \left[1 - \left(\frac{1}{3} \right)^{3-D} \left(1 - \frac{\theta_t}{\beta} \right) \right] \left(1 - \frac{\theta_t}{\beta} \right)^{\frac{2}{3-D}} \quad (12)$$

Recall that C_{KT} is a constant coefficient equal to 56.5 ($C_{KT} = c_{KT}/4$), A is the constant coefficient in the Young-Laplace equation ($=2\gamma\cos(\omega)$), P_a is the air entry pressure, f_f is the fluidity factor ($=\rho g_A/\mu$), θ_t is the critical water content for percolation, and ϕ is the porosity.

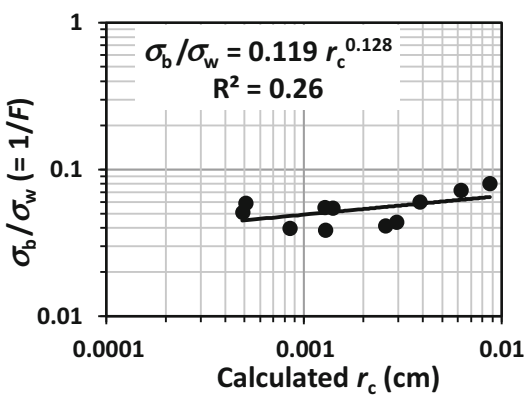
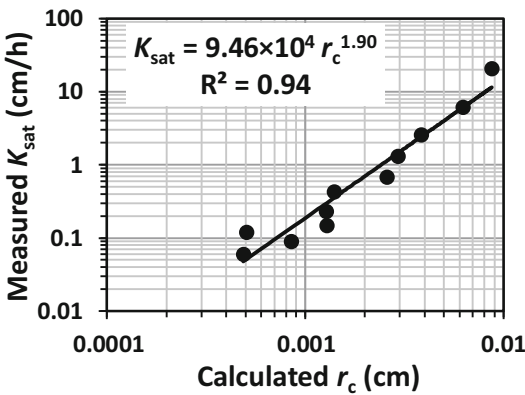
To evaluate Eq. (12), Ghanbarian et al. (2017) used the Rawls et al. (1982) database that included undisturbed cores for 1323 nonstructured soils with 5371 horizons from 32 US states. Rawls et al. (1982) reported the average value of the parameters of Brooks-Corey (1964) capillary pressure model, the total porosity, and saturated hydraulic conductivity for 11 USDA soil texture classes. More specifically, the number of samples and the arithmetic averages of ϕ , θ_r , λ , P_a , and K_{sat} for the Rawls et al. (1982) database are presented in Table 3. The calculated largest accessible pore throat radius $r_{\max}$, the critical pore radius r_c , and the electrical conductivity σ_b/σ_w ($=1/F$) are also given in Table 3. r_c was calculated by Eq. (8) by assuming that $\beta = \phi$, $\theta_t = \theta_r$ and $3 - D = \lambda$ (Ghanbarian et al. 2017). σ_b/σ_w was estimated via Eq. (11) given that $3 - D = \lambda$.

The saturated hydraulic conductivity K_{sat} and the estimated electrical conductivity σ_b/σ_w (or $1/F$) as a function of the calculated critical pore radius r_c are shown in Fig. 4 for the 11 USDA soil texture classes reported by Rawls et al. (1982). As can be observed, although K_{sat} is highly correlated with r_c with $R^2 = 0.94$, σ_b/σ_w does not exhibit strong dependence on r_c ($R^2 = 0.26$). Fitting a power law to the $K_{\text{sat}}-r_c$ and σ_b/σ_w-r_c data yielded exponents slightly less than 2, i.e., 1.9, and slightly greater than zero (i.e., 0.128), respectively. The results are consistent with the fact that water flow is strongly controlled by both geometrical – e.g., pore-size

Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Table 3 The parameters of the Brooks-Corey (1964) model classified by soil texture

Rawls et al. (1982)							$r_{\max}$ (cm) $\times 10^{-3}$	r_c (cm) $\times 10^{-3}$	σ_b/σ_w ($=1/F$)
Soil texture	Samples no.	ϕ^*	θ_r	P_a (cm H ₂ O)	λ	K_{sat} (cm/h)			
Sand	762	0.437	0.020	15.98	0.694	21	9.3	8.7	0.081
Loamy sand	338	0.437	0.035	20.58	0.553	6.11	7.2	6.2	0.073
Sandy loam	666	0.453	0.041	30.20	0.378	2.59	4.9	3.8	0.060
Loam	383	0.463	0.027	40.12	0.252	1.32	3.7	2.9	0.044
Silt loam	1206	0.501	0.015	50.87	0.234	0.68	2.9	2.6	0.042
Sandy clay loam	498	0.398	0.068	59.41	0.319	0.43	2.5	1.4	0.055
Clay loam	366	0.464	0.075	56.43	0.242	0.23	2.6	1.3	0.055
Silty clay loam	689	0.471	0.040	70.33	0.177	0.15	2.1	1.3	0.039
Sandy clay	45	0.43	0.109	79.48	0.223	0.12	1.9	0.51	0.060
Silty clay	127	0.479	0.056	76.54	0.15	0.09	1.9	0.85	0.040
Clay	291	0.475	0.090	85.60	0.165	0.06	1.7	0.49	0.051

(Rawls et al. 1982), as well as the calculated maximum accessible and critical pore-throat radii and electrical conductivity



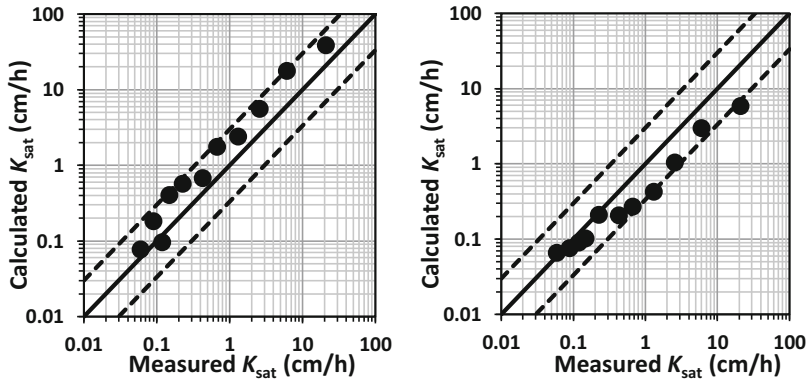
Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 4 Saturated hydraulic conductivity K_{sat} and electrical conductivity σ_b/σ_w as

functions of the critical pore radius r_c for 11 USDA soil texture classes in the Rawls et al. (1982) database

distribution, pore shape, surface area – and topological – connectivity – characteristics of porous media, while electrical current is dominated more by the topology. Comparison of hydraulic conductance $g_h \propto r^4$ with electrical conductance $g_e \propto r^2$ in a perfectly cylindrical tube also confirms that saturated hydraulic conductivity is dominated more by pore space properties than is the case for electrical conductivity.

Figure 5 compares the saturated hydraulic conductivity, estimated by the CPA, Eq. (12), and the Nasta et al. (2013) model with the

experimental data reported by Rawls et al. (1982). Both models estimate K_{sat} within a factor of 3 of the measured conductivity. However, the CPA with $\text{RMSLE} = 0.315$ provided slightly better estimates than the Nasta et al. (2013) model with $\text{RMSLE} = 0.320$. Figure 5 also shows that the CPA-based model overestimated K_{sat} , whereas the bundle of capillary tubes model of Nasta et al. (2013) mainly underestimated it. Interestingly, the CPA estimated K_{sat} of fine-textured soils more accurately than that of coarse-textured ones (see Fig. 5). This is



Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 5 Estimated saturated hydraulic conductivity using (left) the CPA, Eq. (12) with RMSLE = 0.315, and (right) the Nasta et al. (2013) model

with RMSLE = 0.32, versus experimental data reported by Rawls et al. (1982), including 11 USDA soil texture classes. Solid and dashed lines represent, respectively, the 1:1 line and a factor of 3 boundaries

consistent with the main concept of the CPA, which is an appropriate upscaling method for porous media with broad pore throat-size distributions and negligible surface conduction. However, the term “broad” has not been satisfactorily defined in the literature. Regarding the validity of the CPA approach, Shah and Yortsos (1996) stated that, “The basic argument underlying this theory [critical path analysis] is that because of the large exponent in the pore conductance-pore [throat] radius relationship, $g \sim r^4$, natural porous media, even though moderately disordered in pore [throat] size, possess a wide conductance distribution.” Therefore, even for sandy soils whose pore sizes only span one or two orders of magnitude, one may expect the CPA to be reasonably accurate.

It should be pointed out that the CPA is valid when surface conduction is negligible meaning that most of the electric current flows through water in the pores. In the presence of surface conduction, the percolation threshold for electrical conductivity would be small (if not zero) because pore surfaces contribute effectively to electric current but not to water flow. Consequently, the percolation threshold for electrical flow would be less than that for water flow, in contrast to one key assumption in the Katz and Thompson (1986, 1987) model, that the percolation threshold for the two transport mechanisms is the same.

Applications to Packings of Grains

The CPA has been successfully used for estimating the permeability of soils and rock, which typically have broad pore-size distributions (Katz and Thompson 1986, 1987; Ghanbarian et al. 2016a, 2017; Hunt 2001; Hunt et al. 2014; Thompson et al. 1987). Recently, Ghanbarian (2020a, b) evaluated the CPA for estimating fluid flow in uniform sand and glass bead packings, representing homogeneous media with relatively narrow conductance distribution. More specifically, Ghanbarian (2020b) used 105 samples from the literature and compared the CPA estimates of permeability with those from three other models, i.e., the Kozeny-Carman (Kozeny 1927; Carman 1937), Revil-Cathles (1999), and RGPZ (Glover et al. 2006) models.

Estimating k via the three models representative grain diameter ($\bar{D}$). In the literature, arithmetic, geometric, and harmonic means (Porter et al. 2013; Koltermann and Gorelick 1995) have been used to estimate $\bar{D}$. Since in uniform sphere packings with narrow grain-size distributions, the three averages are not greatly different, one may use the arithmetic mean.

In contrast to the Kozeny-Carman model that estimates the permeability by $\bar{D}$ and ϕ , the Revil and Cathles (1999) and RGPZ (Glover et al. 2006) models estimate k based on $\bar{D}$, ϕ , and F , while the CPA model does so based on d_c and F ; see Eq. (5).

If the pore-size distribution of a uniform packing of particles is not available, d_c can be estimated based on $\bar{D}$ and the Ng et al. (1978) relationship. Ng et al. (1978) proposed that for random mono-sized sphere packs with $\phi = 0.4$, the average pore-throat diameter may be approximated by $0.21D$ in which D is the grain diameter. Following Ng et al. (1978), one may set $d_c \approx 2\bar{r}_t = 0.42\bar{D}$ in which $\bar{r}_t$ is the average pore-throat radius. By comparing with experimental data, Ghanbarian (2020b) showed that this approximation yielded accurate permeability estimates for uniform glass bead and/or sand packings. However, the assumption that $d_c \approx 2\bar{r}_t = 0.42\bar{D}$ may cause uncertainties, particularly in packings whose porosities differ substantially from 0.4. More specifically, Ng et al. (1978) reported that $\bar{r}_t = 0.414D$ for simple cubic and mono-sized sphere packs with $\phi = 0.476$, indicating that d_c should be a function of the pore space structure and grain arrangement.

If the value of the formation factor is not available, one may approximate F by $\phi^{-1.5}$, derived theoretically by Sen et al. (1981) for mono-sized sphere packs using the self-consistent model. Recently, Ghanbarian et al. (2016b) proposed a theoretical scaling of Poiseuille's law modified for flow in cylindrical pores with rough surfaces. More specifically, for isotropic systems they derived, $g_h \propto r^{2(4-D_s)-\frac{3-D_s}{2D_s-3}}$ in which g_h is the hydraulic conductance, r is the average pore radius, and D_s represents the surface fractal dimension. For sand and glass bead packings with smooth pore-solid interfaces, one may approximate the pores by cylindrical tubes, assume that $D_s \approx 2$, and, thus, $g_h \propto r^3$. To estimate the permeability using the CPA and Eq. (5), one may accordingly set $c = 72.2$ (see Table 1), as Skaggs (2011) recommended. The assumption $g_h \propto r^3$ was also consistent with water relative permeability estimations in mono-sized sphere packings (Ghanbarian 2020a) and self-similar media in which the pore length is proportional to its radius (Hunt 2001; Hunt et al. 2014).

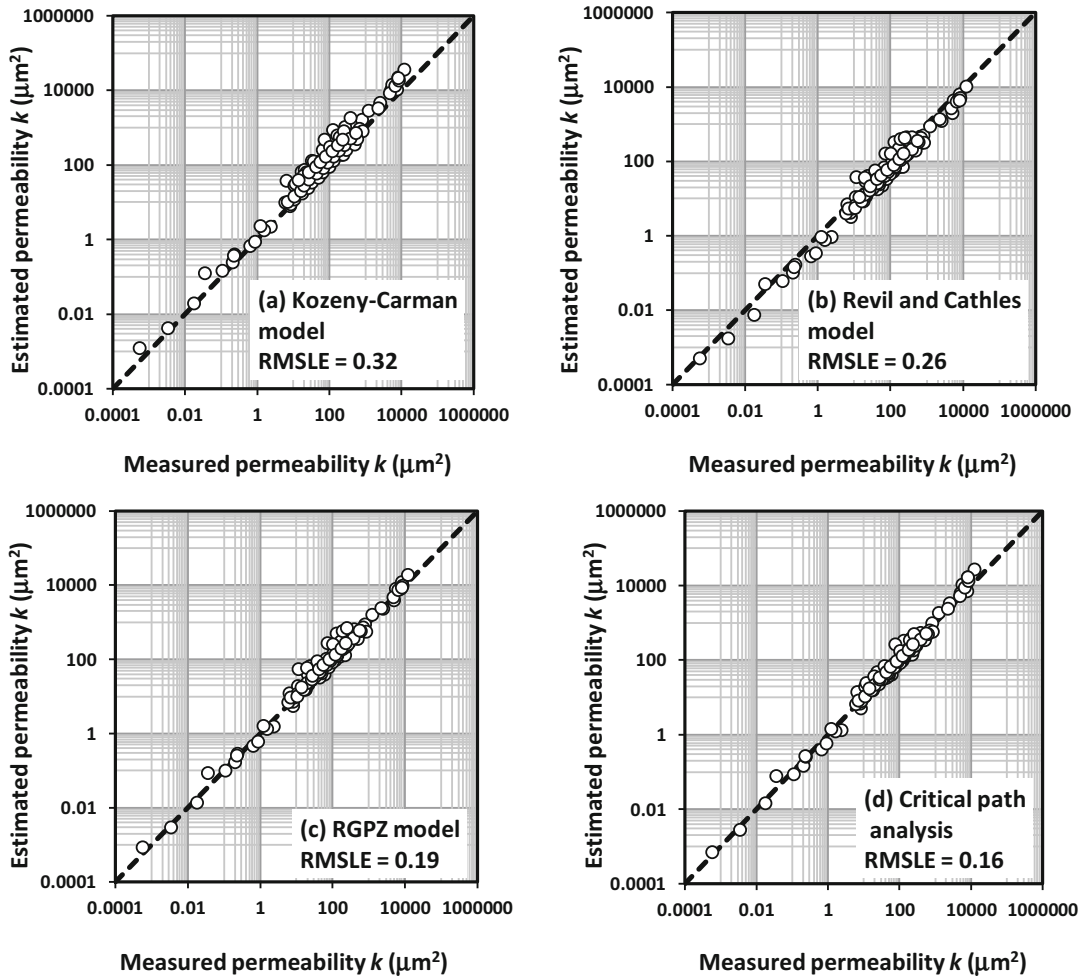
Figure 6 shows the permeability estimates produced by the Kozeny-Carman, Revil and Cathles, RGPZ, and the CPA models, and compares them with the experimental measurements in 105 uniform packings. Generally speaking, although the

Kozeny-Carman model overestimated (Fig. 6a) the permeability, the Revil-Cathles model underestimated k (Fig. 6b). However, the latter estimated the permeability more accurately than the former (RMSLE = 0.26 vs. 0.32). Several studies in the literature (Glover et al. 2006; Mavko and Nur 1997; Van Der Marck 1996; Koch et al. 2012) showed that the Kozeny-Carman model may overestimate the permeability, particularly in media with low porosity. For example, Koch et al. (2012) stated that the Kozeny-Carman model overpredicts the permeability due to its inherent overestimation of the fraction of connected porosity.

Figure 6c and d show the permeability estimates obtained by the RGPZ and CPA models, and compares them with the experimental data for the aforementioned 105 uniform packings, with RMSLE = 0.19 and 0.16 for the RGPZ and CPA models, respectively. Although the permeability estimates are clustered around the 1:1 line, the estimates by the CPA are slightly more precise than the RGPZ's predictions. Glover et al. (2006) also estimated the permeability via the RGPZ and the Kozeny-Carman models and compared the results with measurements for 65 sandstone and carbonate samples. They showed that the RGPZ model with geometric mean diameter results in remarkably more accurate estimates than the Kozeny-Carman model, which mainly overestimated k in consolidated natural porous media.

The porosity of the sand and glass bead packings studied by Ghanbarian (2020b) varied over a relatively wide range, from 0.36 to 0.49. One should note that the relationship $d_c \approx 2\bar{r}_t = 0.42\bar{D}$ was deduced for random mono-sized sphere packings with $\phi = 0.4$ (Ng et al. 1978). As stated earlier, one should not expect $d_c \approx 2\bar{r}_t = 0.42\bar{D}$ to provide accurate estimates of d_c for packings whose porosities differ significantly from 0.4.

Ghanbarian (2020b) demonstrated that the CPA estimated k more accurately than the Kozeny-Carman model (Fig. 6). The former is known to be valid in heterogeneous porous media with broad conductance distributions, while the latter is more suitable for homogeneous and unconsolidated porous materials with narrow grain-size distributions.



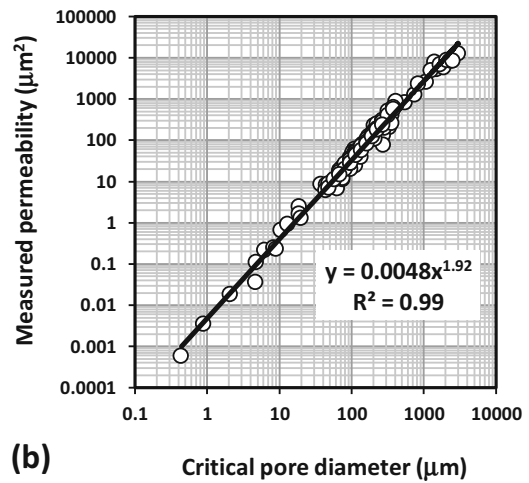
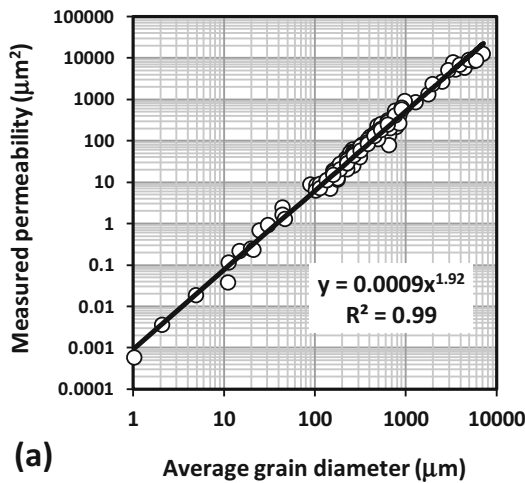
Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 6 Estimated permeability via the (a) the Kozeny-Carman; (b) Revil and Cathles (1999), and (c) RGPZ (Glover et al. 2006) models, and (d) the CPA (with $c = 72.2$), versus measured

permeability for 105 uniform glass bead and sand packings from the literature. The black dashed line represents the 1:1 line. The RMSLE is the root mean square log-transformed error (Ghanbarian 2020b)

As stated before, concepts from the CPA are also applicable to clay-rich media with non-negligible surface conduction. In such materials, in addition to bulk conduction (σ_b), surface conduction (σ_s) may also contribute to the electrical conductivity (Revil et al. 2014). To accurately determine the formation factor and precisely estimate the permeability, one needs to measure electrical conductivity using a highly saline brine so that $\sigma_b \gg \sigma_s$.

In Fig. 7, the measured permeability k as a function of the average grain diameter $\bar{D}$ and

critical pore diameter d_c are presented for 105 packings (Ghanbarian 2020b). The strong correlation between k and $\bar{D}$ had been previously reported in glass bead packings (Beavers et al. 1973; Bryant et al. 1993). Given that the measured permeabilities span over seven orders of variations, the high correlation coefficient $R^2 = 0.99$ is remarkable, and the exponent 1.92 is only 4% less than the theoretical value of 2 in Eq. (5) or (6), which is expected since permeability is proportional to some length scale squared.



Predicting Single-Phase Permeability of Porous Media Using Critical-Path Analysis, Fig. 7 Measured permeability k against (a) average grain diameter $\bar{D}$ and (b)

critical pore diameter d_c for 105 uniform glass bead and sand packings studied by Ghanbarian (2020b)

Conclusions

Concepts from and recent practical applications of the critical-path analysis in the estimation of single-phase permeability of porous media were reviewed in this chapter. Through comparison with experimental measurements in various types of porous media, including tight-gas sandstones, and soils and grain packings, it was shown that the CPA is applicable to a broad range of porous materials. Although, theoretically, the CPA is most accurate in porous media with broad pore-size distributions, it was shown that the approach can estimate permeability reasonably well even in relatively homogenous media with relatively narrow pore-conductance distributions. An important aspect of the theoretical models reviewed here is that no parameters or functions were adjusted for improving agreement with experiment.

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Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock

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Article Outline

Introduction
Theory
Materials and Methods
Results and Discussion
Conclusions
Future Directions
References

Keywords

Surface reaction · Percolation theory ·
Advective solute transport · Transport limited
weathering

Introduction

This chapter combines two topics, conservative solute transport from flowing water in heterogeneous porous media, and chemical weathering of rocks near Earth's surface, that may not ordinarily be perceived as intimately related. But when the characteristics of such solute transport as described in percolation theory are compared with what is known about chemical weathering and soil

formation, a clear correspondence emerges. This progress is a consequence of both advances in observation and experiments about the phenomenon of chemical weathering, and of advances in the theory of solute transport and its application to geosystems at slow and intermittent flow rates. Experiment has also shown that the temporal evolution of chemical weathering and soil formation rates over time are so similar as to suggest that soil formation is limited most strongly by the chemical weathering process. Since the drawdown of atmospheric carbon by chemical weathering of silicate rocks represents the largest sink of atmospheric carbon on Earth (Berner 1992) and since soil sustainability is so important for the success of agriculture (Blanco and Lal 2010; Montgomery 2007a, b), the chemical weathering process has generated significant attention in the last ca. half century.

For nearly 40 years, understanding observed transport of solutes in disordered systems has presented a significant theoretical challenge. Plausible physical assumptions of (i) a transport time, t , proportional to transport distance, x , (ii) exponential decay in the concentration with time (or distance), x , and (iii) a variance, $\sigma^2 \approx t \approx x$, are characteristic of Gaussian transport. But solute transport in heterogeneous porous media as well as related dispersive transport in amorphous semiconductors and polymers (Scher et al. 1991) is, as a rule, not Gaussian (also called non-Gaussian). Actual arrival-time distributions decay slowly and approximately as a power-law, the variance grows approximately as x^2 , and typical particle transport times are superlinear powers of the transport distance (Scher et al. 1991; Berkowitz and Scher 1995).

Absent consensus regarding a theoretical approach, the typical strategy for characterizing non-Gaussian transport has employed descriptions based on, for example, the continuous-time random walk (CTRW) (Scher and Montroll 1975; Scher et al. 1991), and/or the fractional advection-dispersion equation (FADE) (Benson 1998; Benson et al. 2000). However, one needs to fit such models to observed data in order to determine critical model parameters, such as the

power-law arrival time distribution exponent in the CTRW or the fractional exponent in the FADE. Here, we consider a theoretical framework that actually predicts the observed transport from geometrical and topological properties of the fluid within the medium (see e.g., Ghanbarian-Alavijeh et al. 2012).

The possible relevance of transport to the kinetics of silicate weathering has been discussed for decades (e.g., White and Brantley 2003; Maher 2010; Navarre-Sitchler and Brantley 2007, Brantley et al. 1986; Mikesell et al. 2004; Velbel 2011; Muir et al. 1989; Knapp 1989; Schnoor 1990; Casey et al. 1993; Kump et al. 2000; Li et al. 2008; Raoof and Hassanizadeh 2010; Dentz et al. 2011). Traditionally, the limiting transport process considered was diffusion (e.g., White and Brantley 2003; Dentz et al. 2011). Only more recently has fluid flow (advection) been considered as an important transport mechanism for the chemical reactions in weathering processes (Maher 2010; Molins et al. 2012; Salehikhoo et al. 2013). Evidence for the relevance of advection in the functional form of the scaling of chemical weathering can be found in the work of White and Brantley (2003) summarizing time-dependent silicate weathering rates over periods from days to millions of years. These authors showed that the rate at which weathering reactions decay changes significantly after about 1000 years, with the change appearing in the exponent of the power-law dependence on time obtained from fits to field data. At the earlier times, the observed exponent is essentially indistinguishable from that predicted by diffusion-limited reactions (-0.5) (Doering and Ben-Avraham 1988). However, the significant change at $t = 1000$ year is not consistent with diffusion as a limiting factor. Additional evidence for the relevance of advection is reported by Maher (2010), who demonstrates the proportionality of chemical weathering rates to fluid flow rates. Thus, of fundamental importance in what follows, we do not assume that it is the process of diffusion that sets limits on chemical mixing, but rather, spatially variable advection.

Hunt and Skinner (2008, 2010a, b) and Hunt et al. (2011) have formulated a predictive theory of

conservative solute transport based on a statistical description of spatially variable advection through a disordered pore space. This treatment is developed from the cluster statistics of percolation theory, which automatically generates the observed variance $\sigma^2 \approx x^2$ for large transport distances. Since the reactions discussed here include in situ weathering of silicate minerals, the implications of these results are far-reaching. Understanding weathering rates in natural settings helps predict the time scale of soil production since slow kinetics of silicate mineral dissolution allows growth of both vascular plants and vital microorganisms (Maher 2010). It is known that physical denudation and soil production rates are typically proportional to chemical weathering rates (Dixon et al. 2009; Egli et al. 2012, 2014; Hunt and Ghanbarian 2016). With the additional hypothesis that the predicted transport distance (as a function of time) can be identified as a weathering depth (see, e.g., Ma et al. 2012), typical landscape denudation rates are also generated (Yu et al. 2017; Yu and Hunt 2017a) and the approximate time scale for a complete geomorphic reworking of the earth's surface (Anderson and Anderson 2010). In addition, Maher (2010) points out "Slow dissolution of minerals on land and formation of biogenic calcite in the oceans also maintains atmospheric CO_2 concentrations and therefore plays an important role in maintaining global temperatures at levels optimal for the presence of liquid water (Berner 1992). In Earth's past, major changes in rock weathering have coincided with periods of mass extinction (Algeo and Scheckler 1998; Sheldon 2006) and reorganization of global biogeochemical cycles (Raymo 1994; Vance et al. 2009)." Another important application discussed here is to the release of uranium from Hanford sediments, hitherto poorly understood, that can lead to groundwater contamination (Zhong et al. 2005). Additionally, the development of weathering rinds on surface rocks is used for geochronology. The present results appear to put the theory of weathering rind formation on solid footing for the first time.

The chapter is organized as follows. We provide first a brief overview of the theory of advective dispersion and its applicability to weathering

rates. Details of the former can be found in Hunt and Skinner (2008, 2010a), and of the latter in Hunt and Ghanbarian (2016) and Yu and Hunt (2017b). We then survey the extensive datasets used to evaluate the percolation theoretical approach just presented. Detailed comparisons between predictions of the theory and experiment follow in the Results and Discussion.

Theory

Percolation theory provides a theoretical description of the connections defining the fluid flow paths through the medium. Macroscopic properties (e.g., conductivity) are determined from microscale connectivity statistics, often expressed in terms of p , the probability that a given site (pore body) or bond (pore throat) is occupied (e.g., filled with the fluid of interest). Below some critical probability p_c , several small (finite) clusters with different sizes and shapes exist, but connections are too sparse to form a pathway spanning a sample of arbitrary length. As the occupation probability increases toward the critical probability p_c , some individual clusters become connected to each other and make a large interconnected cluster. Above p_c , a spanning cluster forms and percolation across the system occurs. The sample-spanning cluster through which flow and transport take place consists of two parts: (1) the backbone, the multiply-connected part that effectively participates in the transport process, and (2) the dead-end part which carries no flow.

Already in the 1980s Sahimi and coworkers used scaling arguments from percolation theory to indicate that the quotient of the variance and the mean travel distance should be approximately linear in the travel distance (e.g., Sahimi and Imdakm 1988). By scaling, we mean the relationship of a property at one spatial and/or temporal scale to its value at another scale. However, new theory goes beyond scaling arguments (which apply in the limit of large system sizes) and predicts the entire spatial solute distribution and its evolution with time over an enormous range of time scales, and the arrival time distribution at an arbitrary distance from the point at which the

solute is introduced. In the limit of large transport distance, where scaling arguments apply, the predictions of Sahimi and Imdakm (1988) match those of the newer theory.

In the original development (Hunt and Skinner 2008; Hunt et al. 2011) it was assumed that the pore-size distribution of the medium follows the truncated random fractal model of Rieu and Sposito (1991). Details of the model pore-size distribution, for example, the fractal dimensionality of the pore space describing the width of the pore-size distribution, have only minor influence on the behavior that we investigate here (illustrated later in the figures). We apply the simplest model of heterogeneity possible, incorporating only one intrinsic scale of heterogeneity. The distribution of pore sizes (related to local hydraulic conductance values) is monomodal (i.e., a single fractal regime) and of power-law form. However, the details of the pore-size distribution are incidental to the appearance of the solute arrival time distribution, which is affected primarily by percolation exponents, and secondarily by the width of the pore-size distribution, that is, on the magnitude of the heterogeneity.

For the Rieu and Sposito (1991) model, the continuous probability density function for the pore size distribution, $W(r)$, follows a power law given by:

$$W(r) = \frac{3-D}{r_{\max}^{3-D}} r^{-1-D}, \quad r_{\min} < r < r_{\max} \quad (1)$$

where D is the fractal dimensionality of the pore space, r is the pore radius, and $r_{\min}$ and $r_{\max}$ are the smallest and largest pore radii, respectively. As seen next, Eq. (1) generates the Rieu and Sposito (1991) expression for the porosity in terms of $r_{\min}$ and $r_{\max}$. Since the hydraulic conductance, g , is proportional to r^3 in a self-similar fractal medium (Hunt 2001; Ghanbarian-Alavijeh and Hunt 2012), the largest and smallest pore radii of the distribution correspond to minimum and maximum hydraulic conductance values, $g_{\max}$ and $g_{\min}$. Assuming that the pore length is proportional to its radius – a consequence of an assumed fractal (self-similar) nature of the pore space – the volume of each pore is the product of r^3 and a

numerical constant that depends on the precise pore geometry (Hunt 2001). Such a numerical constant can be absorbed into the normalization of $W(r)$ (Hunt 2001), with an integrated value of one over the range of pore sizes.

The porosity ϕ of the medium (proportional to the total pore volume) may be found by integrating $r^3 W(r)$ between limits $r_{\min}$ and $r_{\max}$ to obtain the well-known result,

$$\phi = 1 - \left(\frac{r_{\min}}{r_{\max}} \right)^{3-D} \quad (2)$$

The theoretical description (detailed in Hunt and Skinner 2008) uses percolation theory to quantify the frequency of occurrence of potential solute transport paths that span a system of length x with a given rate-limiting conductance g relative to the critical hydraulic conductance g_c , valid within the range of minimum and maximum hydraulic conductance values, $g_{\min}$ and $g_{\max}$. The critical conductance is found by setting the percolation probability equal to the cumulative probability distribution for local conductances greater than or equal to g_c . The percolation probability depends on the details of the system (Rieu and Sposito 1991), but its primary influence (Hunt and Skinner 2008; Hunt 2001) is on the parameter g_c , and the principle relevance of g_c is to the derivation of the value of a fundamental time scale (Ghanbarian-Alavijeh et al. 2012), which gives the time at which the arrival time distribution has its peak. The probability distribution of the rate-limiting hydraulic conductance, g , for a given distance from the source, x , is then derived in terms of an exponential integral, Ei , as (Hunt and Skinner 2008)

$$W(g, x) \propto Ei \left[\left| 1 - \left(\frac{g}{g_c} \right)^{\frac{3-D}{3}} \right|^2 \left(\frac{x}{L} \right)^{\frac{2}{v}} \right] \quad (3)$$

where L is a fundamental length scale (which for weathering rates on particle surfaces is on the order of a particle or pore size), g_c is the critical hydraulic conductance ($\propto r_c^3$, in which r_c is critical pore radius in the medium), v is the correlation

length exponent from percolation theory (0.88 in a three dimensional system), and $g_{\min}$ and $g_{\max}$ are given by (Ghanbarian-Alavijeh et al. 2012):

$$g_{\max} = g_c \left[\frac{1}{1 - \theta_t} \right]^{3/(3-D)} \quad (4a)$$

$$g_{\min} = g_c \left[\frac{1 - \phi}{1 - \theta_t} \right]^{3/(3-D)} \quad (4b)$$

Here θ_t is the volumetric moisture content at the percolation threshold p_c .

The topology of percolation theory, and the distribution of controlling conductances for $g_{\min} < g < g_{\max}$ are then used to calculate the time that solutes take to travel across the system on such a path. This time, $t(g)$, looks like:

$$t = t_0 \left(\frac{x}{x_0} \right)^{D_b} h(g) \quad (5)$$

where t_0 is a pore crossing time, and x_0 is the fundamental length scale. Because Eq. (5) scales transport times at length scales larger than a pore, we choose x_0 to be equal to a pore length.

$$h(g) = \frac{D}{3-D} \frac{1}{(1 - \theta_t)^{v D_b - v}} \left[\left(1 + \frac{\theta_t}{1 - \theta_t} \right) \left(\frac{g_c}{g} \right)^{1-D/3} - 1 \right] \left[\frac{1}{\left(\frac{g}{g_c} \right)^{1-D/3} - 1} \right]^{(D_b-1)v} \quad (6)$$

where D_b is the fractal dimensionality of the percolation backbone. Results of Lee et al. (1999) indicate that D_b should be the relevant quantity for solute transport, since D_b describes the scaling of typical transport times. Note that $h(g)$ diverges as a power law for $g = g_c$.

The exponents D_b and v obtained from percolation theory are critical to the form of the long-tailed distribution and to the scaling of the solute velocities. Equations (3) and (5) (Hunt and Skinner 2008 and subsequent publications) may be combined to obtain the arrival time distribution, $W(t, x)$ as a function of position, x , using the

probabilistic identity $gW(g, x)dg = W(t, x)dt$, where $W(g, x)$ is given by Eq. (3) and dt/dg is calculated using Eqs. (5) and (6). The factor g , which multiplies $W(g, x)$, makes the solute transport treatment compatible with critical path analysis for the solution of Laplace's equation across the network (in the form of Kirchhoff's laws). The solution for $W(t, x)$ requires a numerical calculation, as given in Hunt and Skinner (2008). An analogous procedure was used to calculate the spatial solute distribution at an instant in time, $W(x, t)$ (Hunt and Skinner 2010b).

At the length scale of a single pore, where the traditional advection-dispersion equation (ADE) is valid (Hunt et al. 2011; Neuman 1990), t_0 is proportional to a distance divided by a fluid velocity, making the expression for solute velocities proportional to pore-scale fluid velocities. In three dimensions and for random percolation (appropriate for fully saturated conditions Sheppard et al. 1999), $D_b = 1.87$. Since $D_b > 1$, the solute velocity is a decreasing function of both time and of solute transport distance. If $h(g)$ could be ignored in Eq. (5), then $x \propto t^{1/D_b}$ and consequently the solute velocity $v = \frac{dx}{dt} \propto x^{1-D_b} \propto t^{\frac{1-D_b}{D_b}}$. For $D_b = 1.87$, the solute velocity $v \propto t^{-0.47}$ scales similarly to diffusion, $t^{-0.5}$, as discussed in the Introduction. However, the presence of $h(g)$ in Eq. (5) alters the form of the solute velocity at larger times, causing it to decay more rapidly than

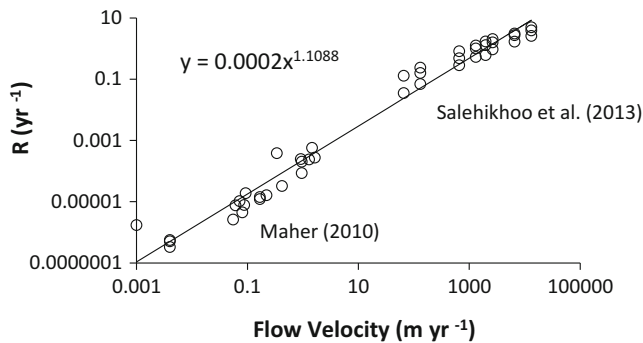
diffusion. This is precisely the change in the reaction rates at larger time scales documented by White and Brantley (2003) (as noted in the Introduction), which is now explained by our theoretical results for solute velocities.

The mean solute velocity is determined as the time derivative of the mean solute position, and can be written in the form,

$$v(t) = \frac{x_0}{t_0} f\left(\frac{t}{t_0}\right) \approx v_0 \left[\frac{t}{t_0}\right]^{\frac{(1-D_b)}{D_b}} \quad (7)$$

where the function f must be determined numerically via the procedure referenced above using the probabilistic transformation. The fundamental fluid velocity in the pore space is $v_0 \equiv x_0/t_0$. The ratio of the solute to fluid velocity is thus $f\left(\frac{t}{t_0}\right) \leq 1$. The proportionality to v_0 , as predicted in Eq. (7), is reflected in experiment (see Fig. 1), in which chemical weathering rates in both the field and in the lab are shown to be proportional to fluid velocities over nearly 7 orders of magnitude of flow rates, from those relevant in the field (measured in the millimeters to meters per year) to those used in experiments (exceeding 10,000 m per year).

The form of the function f turns out to be rather insensitive to the details of the medium, and can be approximated by the power law for the solute velocity given in Eq. (7). This power law



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 1 Experimental (Salehikhoo et al. 2013) and field (Maher 2010) dependences of carbonate and silicate weathering rates, respectively, on flow velocity. Although the near linear flow rate dependence in this figure is continuous from the lowest flow rates (ca. 1 mm year⁻¹) to the

highest (over 10,000 m year⁻¹), this correspondence would not result if the only minerals considered were silicates, as the reaction rate at the highest flow rates would be reaction-kinetics limited. Indeed, even for carbonate minerals (Salehikhoo et al. 2013), the reaction rate likely approaches the asymptotic limit from reaction kinetics at the highest flow velocities

approximation will typically hold for several orders of magnitude of length scale, and up to five orders of magnitude of time scale. Even at longer time scales, f generates a roughly power-law decline in reaction rates that is in accord with similar declines in soil formation rates up to 50 Myr or longer.

The hypothesis here, that chemical reaction rates in natural porous media are solute transport limited, makes them proportional to solute velocities, and provides an additional opportunity to verify the theoretical result in Eq. (7). Yu and Hunt (2017b) have shown how to set up a framework to address simultaneously kinetic and transport limitations on reaction rates, whereby at short time and length scales reaction kinetics sets the primary limitations, but at long time and length scales, reactions are limited by solute transport. The basis of this analysis is the calculation of the Damköhler number, Da_I , which is traditionally (Salehikhoo et al. 2013) given as:

$$Da_I = \frac{\tau_{ad}}{\tau_r} = \frac{\frac{L_0}{v_0}}{\frac{V_p C_{eq} M_g}{R_{exp} A_T}}. \quad (8)$$

Here τ_{ad} is the advection time, τ_r the reaction time, L_0 the column length, V_p the pore volume description of fluid flow rate, C an equilibrium concentration, R_{exp} the *measured* reaction rate normalized by surface area, and A_T the surface area. One difficulty with Eq. (8) is, however, that the solute advection is assumed uniformly equal to the fluid velocity, omitting the slowing of solute advection. Secondly, by putting the measured slowing of the reaction, which is in reality due to the slowed advection, into the kinetics, the result for Da_I does not effectively separate reaction kinetics and solute transport limitations. In fact, as a consequence, Da_I is actually reduced by less efficient advection rather than increased. Our modification (Yu and Hunt 2017b) to Eq. (8) looks like,

$$Da_I = \frac{\tau_{ad}}{\tau_r} = \frac{\frac{L_0}{v_0} * \left(\frac{L_0}{L_p}\right)^{1.87}}{\frac{V_p C_{eq} M_g}{R_0 A_T}}. \quad (9)$$

The quantity L_p is a particle size or pore separation. Because R_0 represents the normalized *well-*

mixed reaction rate, Eq. (9), which is intended to contrast inputs of reaction kinetics with those of solute transport, actually isolates the two effects, rather than mixing them in an uncontrolled fashion as in Eq. (8). In the case that $Da_I \gg 1$, the observed reaction rate is controlled by solute transport and material cannot be chemically transformed faster than its delivery (or removal). Now R is expressed in units of moles/($A \cdot t$) = $(N/N_A)/(A \cdot t) = \rho_M (V/A \cdot t)$ with $\rho_M = N/(N_A \cdot V)$ the molar density, N = number of molecules, N_A = Avogadro's number, V the volume occupied by the reaction products, and V/A the distance to the weathering front, so that $R = \rho_M v$, with v the solute velocity. Consequently, a predicted value for R_{exp} can be expressed in the proxy units of solute velocity, which is equal to the rate of advance of the weathering front. Such a framework generates a quasi-universal, that is, nearly mineral independent, result, with distinctions in reaction rates at a given fluid flow rate mostly traceable to variations in molar density of the constituents. Supporting this conclusion, Yu and Hunt (2017b) then show that Da_I is mostly much larger than 1 for field conditions, and increases moreover with time. Accordingly,

$$R(t) = R_0 f\left(\frac{t}{t_0}\right) = \rho_M v_0 \left[\frac{t}{t_0}\right]^{\frac{(1-D_b)}{D_b}} \quad (10)$$

Here, as in Eq. (7), the approximate equality is valid for up to 5 orders of magnitude in the time scale. The procedure developed so far does not allow a quantitative prediction of R between the two asymptotic dependences at short and long times, but in nature, it turns out that the ability to predict the asymptotic behavior or R in the transport-limited regime is typically sufficient, since this covers all times greater than minutes or hours in most cases (Yu and Hunt 2017b). However, when the implications of Eqs. (7) and (10) for soil formation rates are examined (Egli et al. 2018), it is found that, when field conditions maximally favor limitations due to reaction kinetics (very slowly reacting minerals) and hinder limitations from solute transport (extremely fast fluid flow rates and large pore sizes), such

weathering reactions may be reaction kinetics limited at time scales up to 100 years. This observation adds to the richness of interpretation of field data for weathering and soil formation rates.

Equation (7) can also be transformed so that x is the independent variable using $t \propto x^{D_b}$ from Eq. (5). To the extent that $h(g)$ can be ignored, the approximate power-law result for the reaction rate would be

$$R(x) = \rho_M v_0 \left(\frac{x}{x_0} \right)^{1-D_b} \quad (11)$$

When Eq. (11) is valid, reaction rates decay according to the power $1 - D_b$ (recall that $D_b > 1$). In Table 1 we present the analytical solutions valid for short length and time scales (up to five orders of magnitude of time) for all the elementary functions derived from the scaling of length and time. These simple scaling results will be verified in comparison with over 20 experimental data sets, and were verified in dozens of others not presented here (Hunt and Ghanbarian 2016; Yu et al. 2017; Yu and Hunt 2017b).

Random percolation results are always relevant for saturated conditions. Note that 3D invasion percolation results are expected to be relevant only under drying conditions with the exponent 1.861 appropriate for wetting (essentially the same as for saturated conditions), but 2D invasion exponents should apply for either wetting or drying, an important distinction. In most cases it is assumed that field conditions favoring weathering (vertical water flow) are compatible with either wetting or saturated conditions. The fundamental length scale, x_0 , is taken to be a particle diameter, or pore separation. It is often possible to find t_0 as the time required for fluid to traverse a single pore,

$t_0 = x_0/v_0$, if sufficient information is available to determine v_0 from the experimental data.

For completeness, we consider that one sometimes is interested in the dependence of reaction rates on the measurement scale, rather than the distance of transport. Navarre-Sitchler and Brantley (2007), for example, found a power-law increase of apparent reaction rates with increasing scale of measurement, and interpreted this result in terms of a reaction front with a fractal structure. Percolation theoretical treatments also generate such fractal surfaces, and in principle it is possible to calculate the geometry of such a reaction front within the same theoretical framework that generates the solute velocities. In particular, the perimeter of a percolation cluster in three dimensions has two contributions (Kunz and Souillard 1976; Hunt et al. 2014): one proportional to the square of the radius, and one proportional to the volume of the cluster. Let us define the radius of a large cluster as the correlation length, χ , from percolation theory. In three-dimensional media, the volume of a percolation cluster is proportional to $\chi^{2.5}$ (Stauffer and Aharony, 1994; Hunt et al. 2014). The surface area, A_T , therefore has two terms: one proportional to χ^2 (the square of the radius) and the second proportional to $\chi^{2.5}$ (the cluster volume). Thus we have

$$A_T \approx C \left(\chi^2 + \frac{\chi^{2.5}}{\chi_0^{0.5}} \right) \quad (12)$$

Equation (12) contains an unknown numerical factor, C , and a scale factor, χ_0 . The scale factor represents a length scale above which the fractal properties of the surface of the percolation cluster begin to dominate, and is typically about a factor 10 larger than the fundamental length scale of the heterogeneity (Hunt 2001).

Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock,

Table 1 Power-law scaling of solute transport from percolation theory

Percolation class	Parameter or function				
	D_b^a	$v(x)$	$v(t)$	$t(x)$	$x(t)$
2D random	1.64	$x^{-0.64}$	$t^{-0.39}$	$x^{1.64}$	$t^{0.61}$
3D random	1.87	$x^{-0.87}$	$t^{-0.47}$	$x^{1.87}$	$t^{0.53}$
2D invasion	1.22	$x^{-0.22}$	$t^{-0.18}$	$x^{1.22}$	$t^{0.82}$
3D invasion	1.46	$x^{-0.46}$	$t^{-0.32}$	$x^{1.46}$	$t^{0.68}$

^a D_b values are from Sheppard et al. (1999)

Materials and Methods

We break this compilation into several parts.

We used many datasets available in the literature. These databases are:

- White and Brantley (2003)

These authors reported weathering rate of silicate minerals, in particular, plagioclase, K-feldspar, hornblende, and biotite versus time for both laboratory and field conditions (Tables 4–7 in the original article). The White and Brantley (2003) database covers a wide range of time: 10^{-2} – 10^7 years. For the experimental conditions in their Panola plagioclase experiment, the flow rate of 10 ml/h by gravity flow through crushed granite corresponds to a pore-scale velocity of 16 $\mu\text{m/s}$, which, at about 500 m/year, is some two orders of magnitude larger than for field conditions. Particles were between 250 μm and 850 μm in diameter.

- Maher (2010)

The data are chemical weathering rates of granitic alluvial materials and some sea-floor sediments as a function of fluid residence time in the range of 10^{-3} – 10^5 years, weathering rates versus flow rates as well as surface ages (10^4 – 10^6 years) versus flow rates collected from different published papers. Maher also provides some data for weathering rates as a function of depth, which we digitized and used; these are presented in her Fig. 7.

- Du et al. (2012)

Sediment collected from the Hanford site was sieved into four size fractions: <75 μm , 75–500 μm , 500–2000 μm , and 2000–8000 μm (gravel fraction). A synthetic groundwater with a pH value in the range of 7.8–7.9 was applied to study uranium release from these different size fractions. The data used were concentration as a function of pore volume, which *for constant flow rate* was proportional to travel time.

- Salehikhoo et al. (2013)

Column experiments on magnesite dissolution were performed for various length columns (from 5 cm to 22 cm) and at various flow velocities. The results were reported in terms of the Damköhler number discussed above. The experiments of Salehikhoo et al. (2013) were performed at varying column lengths and flow velocities. These authors demonstrated that the data could be reasonably collapsed to a single curve when represented in terms of their Damköhler number Da_I . However, in their definition of Da_I , they included the observed reaction rate, R_{exp} , generating a circular logic for their conclusion that R_{exp} is a unique function of Da_I . In earlier analyses (Hunt et al. 2015), however, the inconsistency in the analysis of Da_I by Salehikhoo et al. (2013) was missed, leading to a mistaken assumption that Da_I , for constant flow rates, was a proxy for column length. Removal of this error (Yu and Hunt 2017b) allows the more straightforward comparison shown here. In the Salehikhoo et al. (2013) experiments magnesite and quartz were both ground to particles with size range 300–540 μm , leaving a typical particle size (geometric mean) of about 400 μm and typical pore sizes about 30% of that (Gvirtzman and Roberts 1991), or $x_0 \approx 120$ μm . Flow rates ranged from 0.18 m/day to 36 m/day, in other words from ca. 70 m/year to roughly 13,000 m/year, between 1 and 3 orders of magnitude greater than possible for any field results. The fundamental length scale for Salehikhoo et al. (2013) could be calculated from their particle size information.

- Liu et al. (2008)

Liu et al. (2008) measured the desorption of U(VI) from contaminated sediments collected at the Hanford 300 area, the Hanford site. In a small column (10.5 cm length by 2.4 cm diameter) sediments with size of 2 mm and less were packed with a porosity of 0.41. In a large column (80 cm length by 15 cm diameter) cobbles and gravels were also included to investigate the effect of such large particles on U(VI) desorption. From information given, we calculated fluid advection times for single pores, t_0 , to be 0.08 min and 0.19 min, for the short and long columns, respectively. The

columns were saturated from the bottom with synthetic groundwater, and then a constant flow rate was applied to leach the sediments. Particularly with such coarse Hanford sediments, wall flow may not be negligible (Cherrey et al. 2003); investigations (Ghanbarian-Alavijeh et al. 2012) of arrival time distributions (Cherrey et al. 2003) have already shown evidence of 2D unsaturated conditions attributable to wall flow.

- Liu et al. (2009)

These sediments from the Hanford 300 area had been contaminated by U(VI)-containing nuclear fuel fabrication liquid wastes. To study the kinetics of U(VI) desorption, sediment particles less than 2 mm were used. The desorption of U(VI) from sediment was investigated using three U(VI)-free synthetic groundwater (SGW) solutions: SGW2 combination is low pH and carbonate, and high Ca; SGW3 is high in pH and carbonate, and low in Ca; and SGW1 is intermediate between SGW2 and SGW3. In this study, we digitized data of experiments performed under SGW1 and SGW2 solutions. Note that the description of the experimental apparatus does not include flow rates, precluding calculation of t_0 in these experiments.

- Zhong et al. (2005)

The sediment was collected from the Oak Ridge site in eastern Tennessee to investigate the microbial immobilization of groundwater U(VI). Uranium(VI) sorption to the sediment and desorption were performed with and without Fe(II) at different pH values. For the purpose of this study, we considered only the experiments that showed U(VI) desorption under pH = 7.

- Peng et al. (2012)

Uranium and copper concentrations as functions of depth from the surface of an individual basaltic clast were measured by laser ablation. The depths ranged from 0.6 μm to 29 μm . Peng et al. (2012) reported that the copper and uranium concentrations were highly correlated, so we plotted them together.

- Sak et al. (2003)

Detailed chemical analyses of the composition of the outer layers of basalt clasts were performed in order to determine the best analytical definition of a weathering depth. The basalt clasts were located on the surface. Dates were obtained from oxygen isotopic analyses. Sak et al. (2003) concluded that their data were more nearly in accord with a linear increase of rind thickness with time than with a square root increase, thus contraindicating diffusion.

- Pelt et al. (2008)

Analyses similar to those of Sak et al. (2003) were performed on a single basalt clast.

- Ma et al. (2012)

Uranium series isotope compositions and trace element concentrations were analyzed to reveal the rate of increase of weathering rinds in basaltic andesite from Guadelupe Island in a humid tropical climate. These authors noted an increase in the rate of weathering rind development with curvature of the sample, concluding that this increase indicated that the weathering reactions were likely diffusion-limited.

- Oguchi and Matsukura (1999)

Basaltic andesite clasts were collected in a river flood plain from terraces with well-known ages. The thicknesses of a discolored layer (zone I) as well as a zone of chemical alteration (zone II) were recorded. As shown in their Fig. 6, the thickness of the entire weathering rind (zone I + zone II) is 5–10 times the thickness of the brown layer at the surface. The statistics for the mean thickness of the discolored layer for all samples in a given age group were given in Table 2, and these values have been used by other authors to describe the evolution of the weathering rind. When combining these weathering rind data with those of other non-Alpine basaltic materials, we multiplied each value by a numerical constant to optimize the combined

R^2 value. The value of this optimization constant was 2, implying that rind development was about a factor 2 slower.

- Cernohouz and Solc (1966)

Weathering rind data were collected for basaltic crusts in Bohemia. Multiplication of each thickness by a factor 2 allowed representation of the weathering rind thickness as a function of time to be nearly coincident with the tropical weathering rind data.

- Colman and Pierce (1986)

Weathering rinds were measured on basaltic clasts collected from depths of 20–50 cm from the upper parts of the B horizons of soils developed in glacial deposits located near McCall Idaho on the Idaho batholith. More than 1500 measurements at more than 40 sites could be assigned to four distinct age groups, meaning that each age group had upwards of 300 samples.

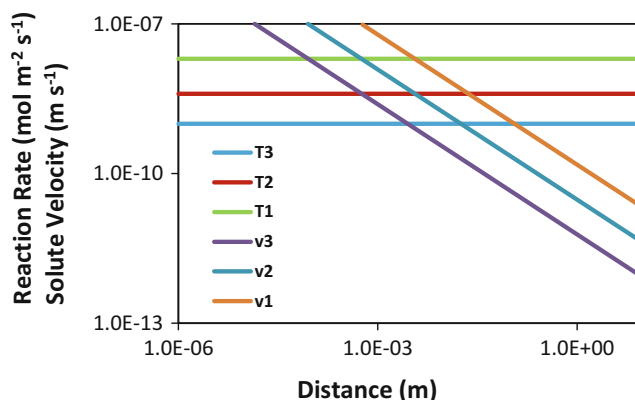
- Deep weathering of bedrock and formation of laterites, bauxites, and saprolites

In a variety of places on Earth weathering of the substrate rocks has proceeded to the point where the rocks have such a high porosity and are bound so lightly that they may often be crushed by hand. The original structure may remain, but the consistency is similar to soil. Such deposits are known by a variety of names, including laterite, bauxite, and saprolite. The value of the data from these sources is predominantly in their extreme age and great thickness, allowing a test of the present equations out to extreme values of time and space. There are associated disadvantages as well, namely the lack of control over climate variables over time periods up to 100 million years, and the typical lack of independent knowledge of erosion rates. However, the formation of such distinct deeply weathered bedrock layers over such long time periods is usually associated with passive continental margins, that is, long-time tectonic stability, and continuously humid climates.

Results and Discussion

Observed reaction rate scaling can be compared with the predicted scaling of solute velocities in many different contexts. Reaction rates may be a function of time, column length, regolith depth, or spatial scale. Soil formation and carbon sequestration rates are both proportional to chemical reaction rates (Egli et al. 2012, 2014; Hunt and Ghanbarian 2016). The dependence of $\langle x \rangle$ on t should describe the advance of the mean weathering front over time, and consequently the temporal scaling of the thickness of weathering rinds or soil depths, too. This suggestion is confirmed for soil depths over time scales from years to 50 Myr in Hunt and Ghanbarian (2016) and Yu and Hunt (2017a).

We start with the question of whether chemical weathering is expected to be transport-limited or kinetics-limited. Figure 2 gives a schematic for understanding this question, a result not greatly different in appearance from Fig. 7 in Maher (2010). In Fig. 3a we show the results of Da_1 calculations for the experiments of Salehikhoo et al. (2013) as well as comparisons with predicted R values as a function of system length for both Salehikhoo et al. (2013) and Maher (2010). We have used the differing flow rates from Salehikhoo et al. (2013) to scale all their data to the same curve, rather than reporting multiple curves. In particular, since it was clear that the data at the slowest flow rates (0.18 m/day) were well within the transport-limited regime, we reduced the measured length scales of more rapid flows by the ratio of the experimental flow rate to 0.18/day. As a consequence, the shortest scaled distances are reduced from 5 cm to about 0.2 mm. A scale of 0.2 mm is, not coincidentally, a bit smaller than the smallest particles (0.3–0.5 mm); at this length scale, Da_1 is 1, and the measured reaction rate is equal to the well-mixed value. One purpose for developing such a scaling plot is to demonstrate that our prediction for R breaks down when Da_1 approaches 1. Thus, our predicted scaling function extrapolates to the well-mixed reaction rate near 1 mm, about a factor 2 larger than the largest particle diameter, and the accuracy of our predictions is compromised at



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 2 Schematic reaction-rate scaling diagram. Horizontal lines give laboratory reaction rates for well-mixed conditions at temperatures $T_3 < T_2 < T_1$, and solute velocities for flow rates $v_3 < v_2 < v_1$. Predicted reaction rates connect horizontal line at given T with diagonal line at given v . In reality, one should expect a smooth cross-over from one

region to the other, but we have not yet been able to derive the form of this crossover, and theory is currently limited to predictions of R in the asymptotic regions and the crossover point at which the asymptotic values for R are approximately equal such that $Da_1 = 1$. Proportionality of a reaction rate to a flow velocity occurs within the transport-limited portion of the diagram

length scales less than 10–15 times a particle separation. The data from Maher fit precisely on the same plot even though the flow rate is different; the data in *her* Fig. 7 extrapolate to her kinetics-limited value at a length scale of 1 mm, exactly as in our figure. In Fig. 3b, we show our calculations of Da_1 and compare our predictions of R with data for fresh Panola plagioclase from White and Brantley (2003), which was digitized from their Fig. 3a, and then represented as a function of length using our scaling relationship for length as a function of time (Eq. (5)). Note that the largest R presented for well-mixed conditions and fresh plagioclase surfaces in Table 4 of White and Brantley is 2.5×10^{-11} mol/m²s. The predicted scaling relationship in Fig. 2b reaches this value at about 1 mm, when Da_1 reaches 1, a length scale ca. 15% larger than the largest particles (850 μ m).

Although the simple power law highlighted in both Eqs. (7) and (11) is verified multiple times, several field observations and experiments show changes of slope at larger time scales, for example, the spatial data of Maher (2010) in Fig. 3a. Since an analogous change of slope, for example, in a dispersivity-length scale plot (see Neuman (1990); Hunt et al. (2011)), has already been observed in the case of the dispersivity, and

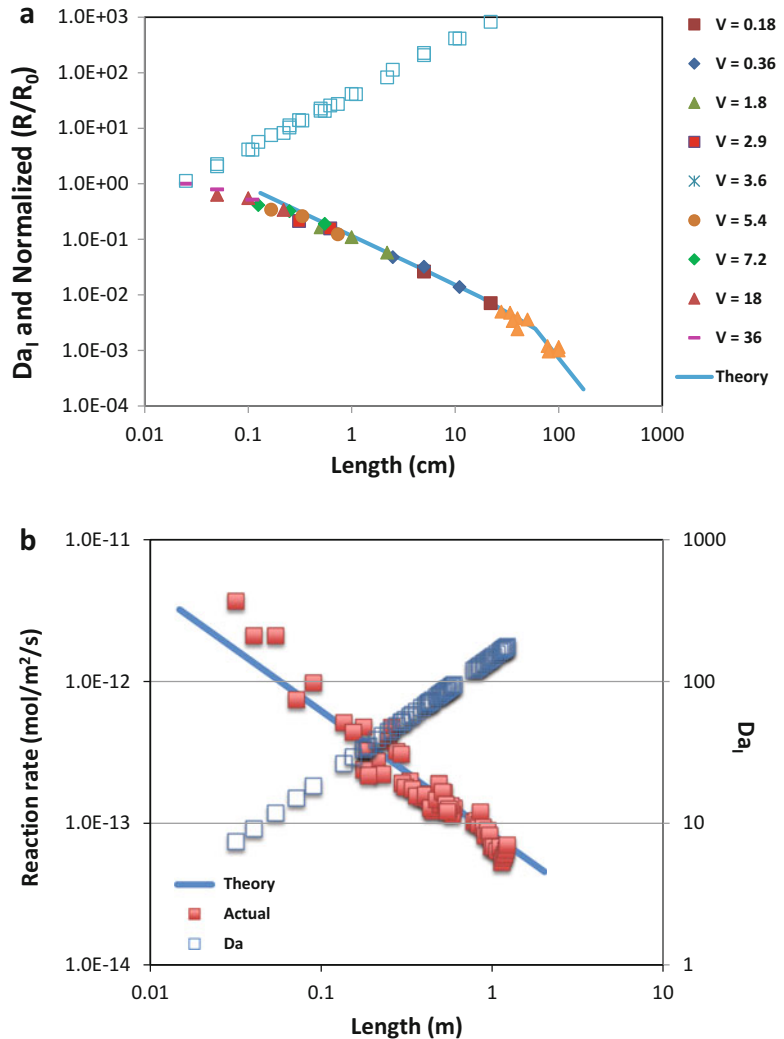
appears in several of the other data sets, we review that result first before considering the other comparisons.

Dispersivity

The dispersivity is most simply represented as the quotient of the variance and the mean distance of travel. The fact that the dispersivity is expressed in the same units as the experimental length scale (meters) allows dispersivity values from different experiments to be represented together graphically without ambiguity. It has been known for nearly 30 years that the dispersivity tends to be 10% of the distance of solute transport (see, e.g., Bear and Cheng (2010) or Gelhar et al. (1992)). In our theoretical treatment, we assumed that the chief influence on the variability of the dispersivity at any given length scale was the magnitude of the heterogeneity of the medium. In the Rieu and Sposito (1991) random fractal model, which we used for calculations, the fractal dimensionality, D , of the pore space describes the width of the pore-size distribution. While D can vary continuously, we only considered two values: $D = 1.5$ describes a relatively narrow range of pore sizes, while $D = 2.95$ can produce variations by orders of magnitude in the

Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock,

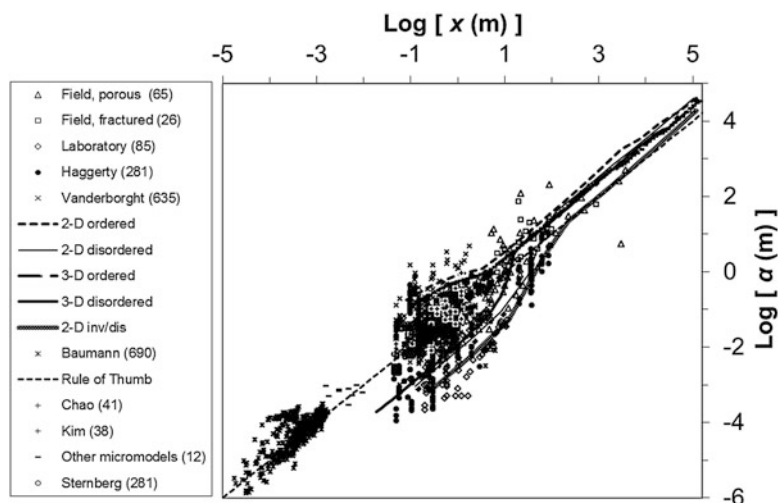
Fig. 3 Panel a shows predicted and observed magnesite weathering reaction rates as a function of spatial scale using Eq. (11) and data from Salehikhoo et al. (2013) and Maher (2010). Numbers in legend are flow velocities in m/day. Calculated Da_i values demonstrate that predictions become accurate only for Da_i values larger than around 10 and at length scales about 10 times the typical particle diameter. Panel b is analogous to panel a, except that the data (fresh Panola plagioclase) are from White and Brantley (2003)



conductance. Approximately 95% of the observed dispersivity values lie within the region bounded by the results for 2D invasion percolation in disordered systems ($D = 2.95$) and 2D random percolation in ordered systems ($D = 1.5$), as shown in Fig. 4. Note that, at field scales, flow might be two-dimensional in layered porous materials, although the medium is three-dimensional, or the flow might be confined to two dimensions by the presence of fractures.

In Fig. 4, identification of the fundamental length scale, called L , as 1 m (relevant to field experiments in solute transport, for typical initial conditions; Hunt and Skinner 2010a) was shown to lead to a change or cross-over in the shape of the

dispersivity curve as a function of length scale at around 100 m, a value previously chosen (Neuman 1990; Neuman and Di Federico 2003), and shown to be in error (Hunt et al. 2011), as representing a fundamental change in sediment architecture. This cross-over in shape of the dispersivity curve is due to a change in the slope of the velocity with time or distance. But mineralogical sources and sinks are heterogeneous at the pore scale, meaning that typical values of the length scale in chemical weathering will tend to be fixed at the particle or pore size, between microns and millimeters, while the cross-over to a steeper slope may thus set on at scales of roughly millimeters to decimeters, depending on actual grain sizes.



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 4 Comparison of dispersivity values from over 2200 experiments from (Haggerty et al. 2004; Neuman and Di Federico 2003; Baumann et al. 2002; Pachepsky et al. 2000; Chao et al. 2000; Kim et al. 2002; Haggerty 2001; Seaman et al. 2007; Sternberg et al. 1996; Vanderborght and Vereecken 2007; Danquigny et al.

2004) for the same variability in heterogeneity as in Figs. 2, 3, 4, and 5. The number in parentheses is the number of experiments. “Disordered” stands for $D = 2.95$, while “ordered” stands for $D = 1.5$. “Inv” stands for invasion percolation (relevant for unsaturated conditions); all others are random percolation (saturated conditions?). A reasonable envelope of dispersivity values is represented by the theoretical variability shown

Comparison with Weathering Rind Development

Since weathering rind thickness effectively measures the solute transport distance, rather than the weathering rate, in the following we compare experimental results with the exponents from the last column in Table 1. With one exception (random percolation relevant to saturated conditions and invasion percolation to unsaturated cases), we find that weathering rind development is consistent with invasion percolation exponents. We thus infer that weathering rinds develop predominantly under unsaturated conditions.

It has been noted that “many studies of [the thickness of basalt] weathering rinds indicate a $t^{0.8}$ dependence (Navarre-Sitchler et al. 2007) rather than the $t^{0.5}$ dependence from diffusion.” The first dependence matches the prediction for weathering rind development for 2D flow under unsaturated conditions ($t^{0.82}$; Table 1), and the second matches the prediction for 3D flow under saturated conditions ($t^{0.53}$; Table 1), allowing a unifying interpretation in terms of advective solute transport. But other functional dependences have also been

proposed as relevant. We show that many of the alternates, and perhaps most, are compatible with an interpretation based on solute advection.

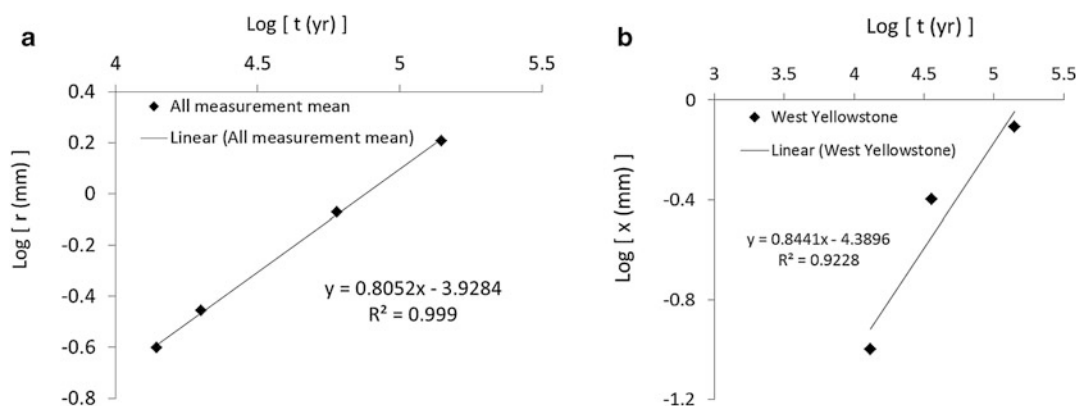
In order to understand this uncertainty, we reproduce (with some additions) a table from Sak et al. (2003).

Consider several specific table entries. Moore (1966) investigated submarine basalt clasts from Hawaii and obtained a weathering rate thickness that increased as $t^{0.5}$, interpreting the results as diffusion limited. But the fact that the basalts were submarine means that they were necessarily saturated. For random percolation (saturated conditions) in 3D, the exponent 0.53 from the last column of Table 1 is compatible with the reported value of 0.5. The logarithmic function for the weathering rinds reported by Colman and Pierce (1986) from McCall ID (Idaho) was actually not obtained from experiment, but chosen on the basis of their earlier results for West Yellowstone. We obtained the rind ages from the table in their Fig. 2, and the mean values of all their rind thicknesses from their Table 1 is shown in our Fig. 4a. It is noteworthy that each mean has been taken

over measurements of 300–400 clasts. Their data conform well to a power law interpretation because use of this phenomenology returns $R^2 = 0.999$. The data from West Yellowstone shown in Fig. 4b do not conform as well to a power law. However, the powers extracted from the data in Fig. 5a and b are quite similar, 0.805 and 0.844, supporting the power-law interpretation. Comparison with the entry in the third row of Table 1 for the exponent in the relationship for $x(t)$ (0.82) shows that Colman and Pierce (1986) scaling exponents imply 2D flow under unsaturated conditions (where invasion percolation is relevant). Other data from Alpine sites (Chinn 1981; Knuepfer 1994) yield similar exponents (0.76, 0.81, and 0.86). Given the assumption of Colman and Pierce (1986) that the same logarithmic phenomenology was appropriate for all their sites, it is quite possible that the same power-law (0.82) is appropriate for all Alpine sites. The consistency of exponent values near 0.82 obtained in Alpine environments suggests that fracture flow could provide 2D connectivity. In such environments intense solar radiation, large diurnal temperature fluctuations, and freeze/thaw cycles contribute to formation of micro-fractures in rocks.

We should note at the outset that observed thicknesses of weathering rinds tend to increase from about 1 mm at around 10,000 years to ca. 1 cm at time scales exceeding 100,000 years. In contrast, soil thicknesses typically reach decimeters by

thousands of years and meters by 100,000 years. The distinct values of the scaling exponents complicate the comparison somewhat, but we can understand this contrast relatively simply when considering the role of the fluid flow rate in determining the time scales. In the subsurface, the rate at which surface fluids infiltrate is $(P - \text{AET} + \text{run-on} - \text{run-off}) / \phi$, where ϕ is the porosity, and is typically on the order of 0.3 m/year worldwide (Yu and Hunt 2017b, based on summaries of Lvovitch 1973). Here P is precipitation and AET is actual evapotranspiration. But the rate at which these fluids actually penetrate a buried clast is reduced, due to their parallel configuration with the soil, by the ratio of the hydraulic conductivity of the clast to that of the soil. For unfractured basalt, typical K values are about 3.4×10^{-8} cm/s, (British Geological Survey) <http://nora.nerc.ac.uk/7457/1/CR06160N.pdf> (or about an order of magnitude lower, http://www.aqtesolv.com/aquifer-tests/aquifer_properties.htm) whereas for unconsolidated media, typical K values are closer to 10^{-4} cm/s, or somewhat larger (http://www.aqtesolv.com/aquifer-tests/aquifer_properties.htm). Thus, one finds, using an exponent 0.82 (0.53), a more than three (two) order of magnitude thinner weathering rind in basalt than the thickness of the soil under identical climatic conditions, explaining the contrast between meter soil depths and millimeter to centimeter rind thicknesses. Analysis of surface clasts is somewhat more complex,



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 5 Panel a shows weathering rind data of Colman and Pierce for the McCall site, while panel b shows their

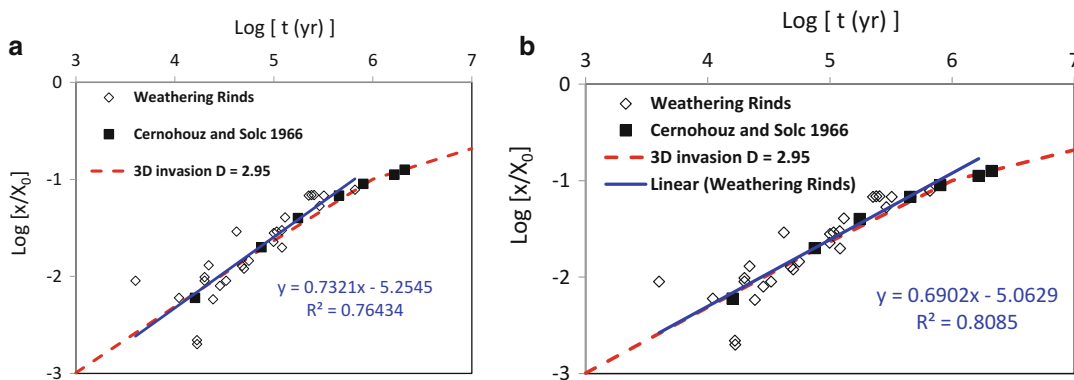
data for the West Yellowstone site. The McCall site data are in excellent accord with theory for 2D flow under unsaturated conditions predicting weathering rind thickness should increase as the 0.82 power of the time

but with K values orders of magnitude smaller than precipitation rates, nearly all precipitation will run off, rather than penetrate, the clast surface.

We present the basalt weathering rind data of Sak et al. (2003) together with other basalt data from Ma et al. (2012), Pelt et al. (2008), Oguchi and Matsukura (1999), Navarre-Sitchler et al. (2011), and Cernohou and Solc (1966) in Fig. 6. Most of these studies were conducted in tropical climates; the data for rind thickness in the two exceptions (Oguchi and Matsukura (1999) and Cernohou and Solc (1966)) were obtained from temperate sites. It is known (Sak et al. 2003) that weathering rind development in tropical climates is faster than in temperate regions. Since we have assumed reaction rates are proportional to fluid flow rates, and these are very sensitive to moisture content, we would expect tropical weathering rinds to develop faster. In order to raise the data from the temperate sites to the same level, these had to be multiplied by a constant factor of 2, consistent with typical tropical flow velocities in weathering rinds that are a factor roughly 2 larger than those in temperate regions.

If the last two points in the Cernohou and Solc (1966) data (at over 1 Ma) are neglected (Fig. 6a), the extracted power for all six data sets is 0.69, compatible with 3D flow under unsaturated conditions (0.685). The R^2 value is 0.81, rather high for simultaneous comparison of six different data sets. If the Cernohou and Solc (1966) data set is dropped altogether (Fig. 6b) the extracted power rises to 0.73, and the R^2 value falls to 0.74. The neglect of the last two points in this context is further supported by the discussion below.

Note that if the last two points of the Cernohou and Solc (1966) data are reinserted, the entire data set is then also in accord with the predicted weathering rind development curve for the case $D = 2.95$ (with 3D invasion percolation exponents), at least for the right choice of t_0 . Such a reduction in weathering rind development rates commencing at several hundred thousand years is generally compatible with reductions in weathering rates in other contexts that we discuss below, and predicted using the identical model of the medium.



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 6 Weathering rind data from Sak et al. (2003), Ma et al. (2012), Pelt et al. (2008), Oguchi and Matsukura (1999), Navarre-Sitchler et al. (2011), and Cernohou and Solc (1966). The results from Oguchi and Matsukura (1999) and Cernohou and Solc (1966) were obtained from experiments in temperate climates, the remaining data sets from tropical climates. Since the rates of weathering in temperate climates were roughly a factor of

2 slower, the data from these sources were multiplied uniformly by this factor in order to make them compatible with the remaining data. On a double logarithmic plot, this simply raises those two data sets uniformly. In 6a the data from Cernohou and Solc (1966) are not included in the regression, while in 6b they are. Inclusion of this data in the regression reduces the discrepancy between the predicted and observed values of the exponent from 7% to less than 1%

Comparisons with Weathering Data Summaries

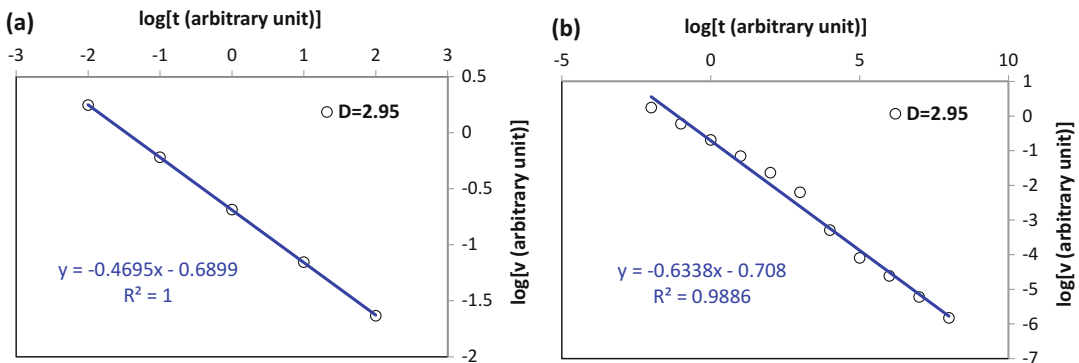
Weathering rates of silicate minerals in the earth's crust are believed to decay according to power laws. The decay rate over shorter time intervals (from months to about a decade) is reported as $t^{-0.51}$, while at geologic time scales, exceeding 10,000 years, the power is reported as $t^{-0.61}$ (White and Brantley 2003).

Our analytical result for 3D random percolation (Table 1) is $v \propto t^{-0.47}$, valid at short time scales. In fact, at such short time scales (up to years) our numerical solutions of the velocity as a function of time (shown in Figs. 7a and 8a with $D = 1.5$ and 2.95, respectively) yield $v \propto t^{-p}$; $p = 0.49 \pm 0.02$, which does not differ greatly from the analytical solution, though it is closer to results obtained from fresh Panola plagioclase (White and Brantley 2003) (shown in bold as $R \propto t^{-0.51}$ in Table 2). At longer time scales (Fig. 7b with $D = 1.5$ and Fig. 8b in which $D = 2.95$), through about a million years, theory generates a different result for the scaling of the velocity, namely $v \propto t^{-q}$, with $q = 0.61 \pm 0.02$ (underlined in Table 2). In field observations, roughly double the uncertainty (i.e., 0.04) in the power results, if this uncertainty is obtained by comparison of the various silicates tested. In both results from our numerical calculations, the uncertainty in the exponents derives from the wide range of possible distributions investigated for the heterogeneity, that is, conductance (as in permeability).

Comparison with Scale-Dependence of Weathering Rates

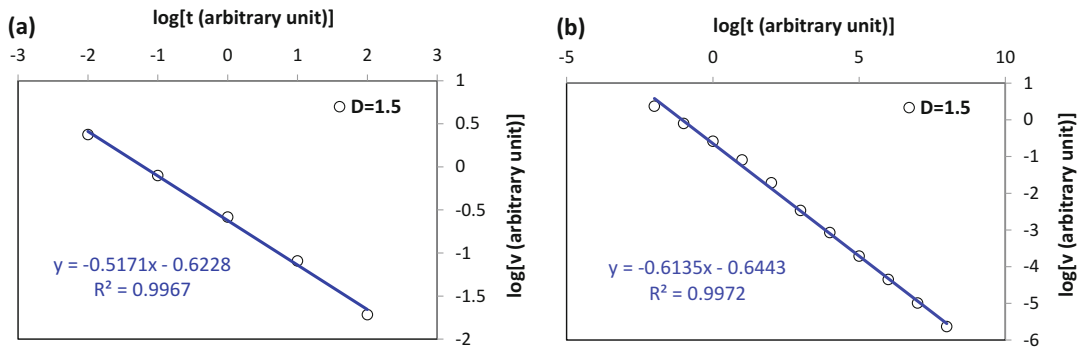
The analysis of Navarre-Sitchler and Brantley (2007) yielded an *increase* in reaction rate with measurement scale. They suggested that this increase was due to the fractal structure of the reaction front and the corresponding increase in surface area with increasing scale. In their Fig. 3, they find that the reaction rate increases as the 0.33 power of the measurement scale. Navarre-Sitchler and Brantley's (2007) interpretation in terms of a fractal surface allowed extraction of a surface fractal dimension $D_s = 2.33$. But if percolation clusters can be utilized to predict the reduction of reaction rate with increasing time, then their fractal surfaces should also provide for an increasing area of a reaction front with spatial scale.

Consider alternatively the percolation treatment, Eq. (12) with specified fractal dimensionality. The linear dimension of a nitrogen molecule is on the order of 10^{-7} mm (Navarre-Sitchler and Brantley 2007). In accord with the conclusions of Hunt (2001) we choose a fundamental length scale an order of magnitude larger, that is, 10^{-6} mm. Using $C = 10^{-5.5}$, which sets a vertical scale (the same choice as in Navarre-Sitchler and Brantley 2007), we then generate the comparison in Fig. 9. This figure also shows the result of Navarre-Sitchler and Brantley (2007). Although their single power appears to fit the data somewhat



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 7 (a) Determination of the exponent of the power law for the solute velocity as a function of time over the

first five orders of magnitude of time scale. (b) Determination of the exponent over the entire ten orders of magnitude of time scale. Media with wide ranges of local hydraulic conductances are chosen ($D = 2.95$)

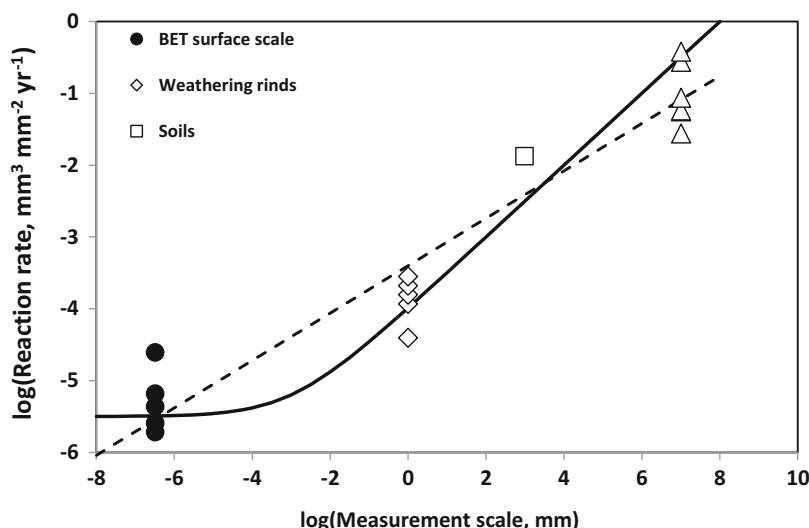


Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 8 (a) Determination of the exponent of the power law for the solute velocity as a function of time over the

first five orders of magnitude of time scale. (b) Determination of the exponent over the entire ten orders of magnitude of time scale. Media with narrow ranges of local hydraulic conductances are chosen ($D = 1.5$)

Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Table 2 Empirical models for rind development, r , as a function of time

Relationship	Equation	Reanalysis	Parent material	Study area	Reference
Logarithmic	$r = 4.64 \times \log(1 + 10^{-5} t)$	$t^{0.69}$	Basalt	Bohemia	Cernohouz and Solc (1966)
Logarithmic	$r = \log(0.73 + 3.8 \times 10^{-5} t)$	$t^{0.844}$	Basalt	W. Yellowstone	Colman and Pierce (1981)
	$r = \log(0.73 + 8 \times 10^{-5} t)$		Basalt	MT	Colman and Pierce (1981)
	$r = \log(0.73 + 3 \times 10^{-4} t)$		Basalt	Yakima	Colman and Pierce (1981)
	$r = \log(0.73 + 7 \times 10^{-5} t)$	$t^{0.805}$	Basalt	McCall ID	Colman and Pierce (1981)
	$r = \log(0.73 + 5.8 \times 10^{-5} t)$		Andesite	WA	Colman and Pierce (1981)
	$r = \log(0.73 + 8.2 \times 10^{-5} t)$		Andesite	Truckee	Colman and Pierce (1981)
	$r = \log(0.73 + 1.7 \times 10^{-4} t)$		Andesite	Lassen/Rainier	Colman and Pierce (1981)
Power law	$r = 0.00373 t^{0.806}$	$t^{0.806}$	Sandstone	New Zealand	Chinn (1981)
Power law	$r = 0.001 t^{0.75}$	$t^{0.75}$	Sandstone	New Zealand	Knuepfer (1994)
	$r = 0.00099 t^{0.86}$	$t^{0.86}$			
Relaxation	$r = 8.7(1 - \exp(-t/10.53))$		Sandstone	New Zealand	Whitehouse et al. (1986)
Diffusion	$r = A t^{0.5}$	Advection	Submarine	Hawaii	Moore (1966)
			Obsidian		Friedman and Long (1976)
			Hydration		Friedman and Smith (1960)
Linear	$r = B t$	$t^{0.69}$	Basalt	Costa Rica	Sak et al. (2003)
Linear	$r = B t$	$t^{0.69}$	Basalt	Costa Rica	Navarre-Sitchler et al. (2011)



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 9 The dependence of reaction rates on the scale of the measurement from data compiled by Navarre-Sitchler and Brantley (2007). Watersheds are plotted as open triangles, soil profile scale as open squares, and weathering

rinds as open diamonds. BET surface area-normalized laboratory rates are plotted as closed circles. The straight line is the interpretation of Navarre-Sitchler and Brantley (2007) in terms of a surface fractal dimensionality $D_s = 2.33$, while the curve is the percolation theoretical prediction

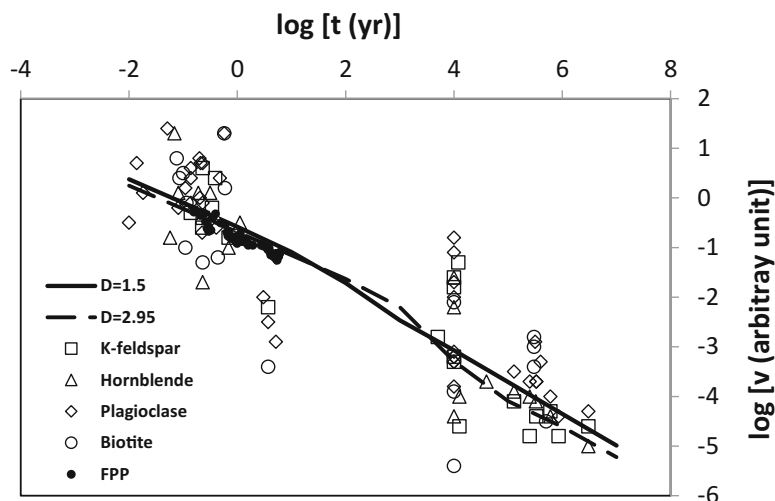
better, our comparison involves only a single adjustable parameter, that is, the vertical scale, rather than the two parameters they used (fractal dimension and numerical prefactor). More generally, if experimental values are known only at three different length scales, a function that is the sum of two such powers may be difficult to distinguish from a single power, particularly in the case of considerable scatter.

Direct Comparison with Weathering Rate Data

Here we compare the derived velocity, $v = v_0 f(t/t_0)$, as a function of time with the rates of weathering of mineral surfaces, as illustrated in Fig. 10. The two theoretical curves generate the predicted variability in reaction rates associated with variations in the heterogeneity of the subsurface ($D = 1.5$ to $D = 2.95$). All the data presented are from White and Brantley (2003). White and Brantley (2003) include some laboratory experimental data (fresh Panola plagioclase) with the remaining field data that they collected from many sources. However, the experiment was conducted under conditions that were meant to be compatible with those from the field.

The fundamental time scale depends on the flow velocity. Field weathering processes typically occur under gravity flow. White and Brantley's (2003) column experiment on fresh Panola plagioclase simulated gravity flow: "column reactors ... are easily designed as passive gravity flow systems. ..." With a typical hydraulic conductivity of near surface crustal materials on the order of 10^{-4} cm/s (Anderson and Anderson 2010) one finds typical vertical flow velocities $v_0 \approx 1 \mu\text{m/s}$ under saturated conditions (or about $5 \mu\text{m/s}$, in the summary of Bloesch and Sivapalan (1995)). Bloesch and Sivapalan (1995) also suggest that the dominant variability of flow velocities is two orders of magnitude centered on this value. However, flow rates in the field, when averaged over a year, cannot greatly exceed precipitation rates, which tend to average less than a meter worldwide, meaning that experimental flow rates are, as a rule, much higher than field values.

The data in Fig. 10 are taken directly from Tables 4–7 of White and Brantley (2003), except for fresh Panola plagioclase data (which were digitized from their Fig. 3a). The actual figure is plotted exactly as in their Fig. 6. If rates are



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 10 Comparison of the numerically obtained solute velocity as a function of time with weathering rates, both over nine orders of magnitude in the time scale. Data for weathering rates compiled by White and Brantley (2003).

FPP stands for Fresh Panola Plagioclase, a reference to laboratory experiments conducted over 6 years. Theoretical examples for both a relatively homogeneous medium ($D = 1.5$) and a heterogeneous medium ($D = 2.95$) are shown

proportional to solute velocities as hypothesized, the vertical scale can be interpreted either as R or v_0 . For the data, the fundamental time unit is years. In our calculations, we used $t_0 = 10^{-2}$ year = 4 days, consistent with “Transport limitation appears to begin as fluid residence times exceed approximately 2 days” (Maher 2010). The dimensions of the Panola column were 100 cm length and 2.4 cm diameter. With 750 gm of granite and a density of 2.7 g/cm^3 , one obtains a porosity $\phi \approx 0.4$. At the given volume flux of 10 ml/h through this column, mass conservation gives a pore-scale fluid velocity of about $15 \text{ } \mu\text{m/s}$. In the transport limited regime, reaction rates are shown by Maher (2010) (her Figs. 4 and 5) to be proportional to flow rates, v_0 . Navarre-Sitchler and Brantley (2007) estimated that, for field weathering data, if the variability due to temperature is accounted for, about two orders of magnitude of uncertainty remains, an uncertainty indicated in Fig. 10. However, a two order of magnitude uncertainty in flow rates, and equal uncertainty in the value t_0 , equates to a one order of magnitude variability in $R(t)$. Consequently, we might attribute most of the variability that lies outside our range of expected values to a lack of control of the temperature variable.

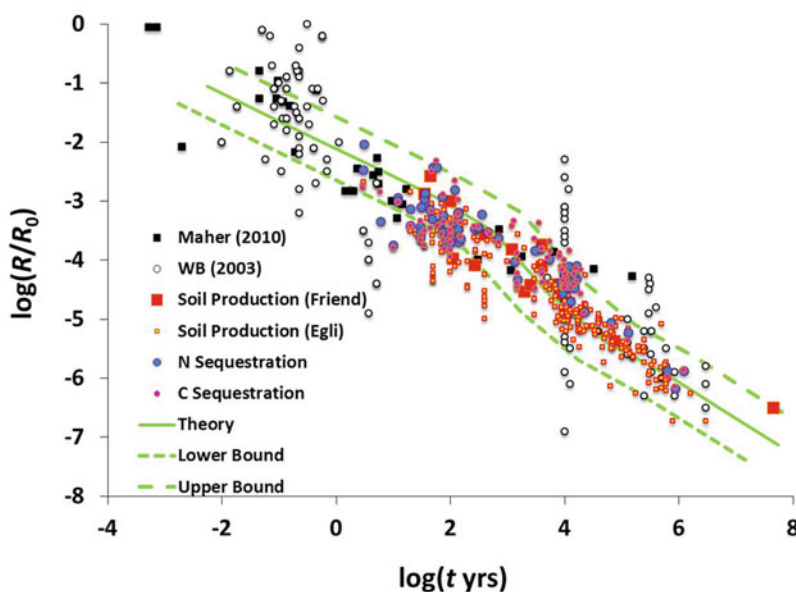
Considering that the data at around 10,000 years, which show the greatest variability, were taken from sites around the margins of the rapidly retreating ice sheets (data entries in Tables 4–7 of White and Brantley 2003), such an interpretation appears reasonable. However, this potential suggestion is not meant to exhaust the possible explanations for the discrepancies particularly in this time frame.

We can also show that the absolute experimental times of the White and Brantley (2003) experiment are consistent with the theory. Given (White and Brantley 2003) that the particle sizes in the fresh Panola plagioclase experiment range from 0.25 mm to 0.85 mm, one can estimate a typical pore radius as 0.3 times the typical particle radius (Gvirtzman and Roberts 1991), or about 0.15 mm. Thus a typical pore crossing time is about $150 \text{ } \mu\text{m} / 15 \text{ } \mu\text{m/s} = 10\text{s}$. With a column length of 100 cm, one can find between $1000/0.85 = 1176$ and $1000 / 0.25 = 4000$ particles along the length of the core, and a similar number of pores. Core solute *transit* times of between (10s) $(1176)^{1.87} = 0.17 \text{ year}$ and (10s) $(4000)^{1.87} = 1.7 \text{ year}$ would be expected, comparable to the time values in the experiment (White and Brantley 2003) that range from 0.19 year to 6.2 year.

Maher (2010) has incorporated data unavailable to White and Brantley (2003). In her Fig. 2, Maher (2010) plots data for the dependence of reaction rates on fluid residence time. The range of time scales is from hours to about 100,000 years. Over this time range, the reported reaction rates decline according to the -0.53 power of the residence time. In our Fig. 11, we compare our predictions with the data of Maher (2010) and White and Brantley (2003) simultaneously. We have also added in data for C and N sequestration rates (Egli et al. 2012) together with soil formation data (Egli et al. 2014; Friend 1992). We have again used $D = 2.95$ with exponents from three-dimensional random percolation in the comparison, implying that the weathering occurred under saturated conditions. Note that Maher (2010) distinguishes between thermodynamic controlled and transport controlled regimes in these data, but the distinction appears here to be unnecessary.

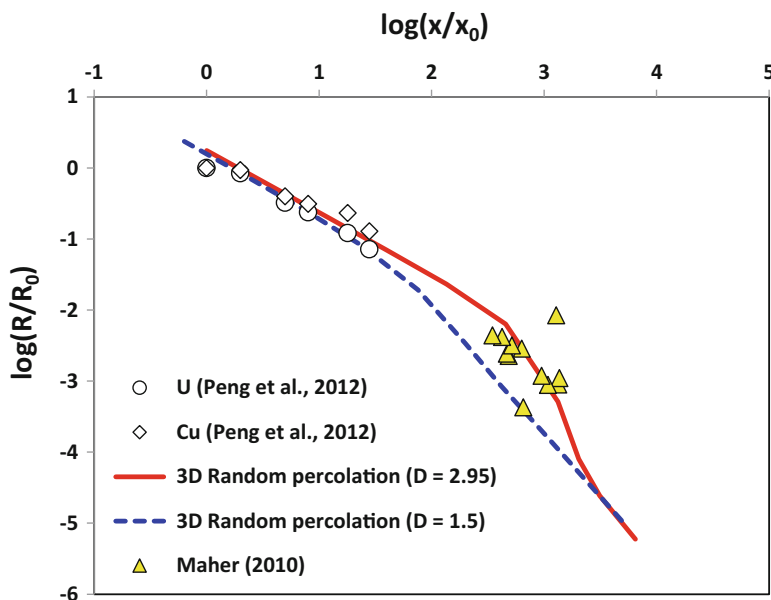
Maher (2010) shows in her Fig. 7 that observed reaction rates decline approximately as the soil thickness raised to the -0.9 power (for thicknesses of roughly 10 cm to 1 m), as one would expect from using the thickness of the soil cover as an equivalent measure for the transport distance, x . Solute velocities are proportional to $x/t \approx x/x^{D_b}$ from Eq. (5), giving $x^{-0.87}$. This prediction agrees well with Maher's experimental result.

We now compare data from Maher's (2010) Fig. 7 and from Peng et al. (2012) for the length dependence of the reaction rate with theory in our Fig. 12 and find excellent agreement, again for 3D random percolation and pore-space fractal dimensionality 2.95. Putting all results on the same plot (Fig. 12) requires one to evaluate the scale constants, x_0 and R_0 , for *each* set of data. A fundamental "surface controlled" reaction rate of $10^{-2.3} \text{ year}^{-1}$ is assumed in Maher (2010), which we assign to R_0 for her data. In her Fig. 7, the collected data for the spatial scaling of reaction



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 11 Simultaneous comparison of theoretical solute velocity as a function of time with weathering rates as a function of fluid residence time from Maher (2010) and age from White and Brantley (2003), as well as with data for soil production from Egli et al. (2014) and from Friend

(1992), and finally for C and N sequestration rates from Egli et al. (2012). In the cases of the C and N sequestration rates, it was necessary to choose an initial rate without specific guidance from the authors. The time scales are all identical. Uncertainties in predictions relate to spreads in commonly observed flow rates in the field (from about a decimeter to about 10 m per year)



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 12 Reaction rates from experiments and field data are compared to theoretical predictions as a function of length scale over 6 orders of magnitude of distance (four orders of magnitude of scaled distance, x/x_0). Experimental data are from laser ablation studies of the depth dependence of uranium and copper concentrations from a single particle (Peng et al. 2012). Field values are digitized from

Fig. 7 in Maher (2010). The experimental reaction rate from Peng et al. (2012) is normalized to the initial uranium and copper concentrations (at or near the surface). Normalization for the field data (2010) is to the given initial value of $10^{-2.3}$. Experimental and field data are presented together using distinct values of x_0 : $x_0 = 1 \mu\text{m}$ for intraparticle data but 0.75 mm for the interparticle data of Maher (2010). The calculations of these values are described in the text

rates extrapolate to $10^{-2.3} \text{ year}^{-1}$ at about 1 mm . Using the flow rate of 0.05 m/year (from Maher (2010) Fig. 7), assumed relevant for these data, and a fundamental time scale of about 10^{-2} year (from Maher (2010) Fig. 2), one finds a fundamental length scale about 0.5 mm . We used the mean of these two values to set the fundamental length scale, $x_0 = 0.75 \text{ mm}$, for the data from Maher (2010). Peng et al. (2012) measured uranium and copper concentrations as functions of depth from the surface of an individual basaltic clast using laser ablation. The depths ranged from $0.6 \mu\text{m}$ to $29 \mu\text{m}$. Peng et al. (2012) reported that the copper and uranium concentrations were highly correlated, so we plotted them together (Fig. 12). For this purpose, we had to normalize both the copper and the uranium depths and rates to their initial values generated at a depth of about $1 \mu\text{m}$. These two data series are nearly indistinguishable and are plotted together.

Weathering Summary

In the following discussion, we apply the hypothesis relating solute transport distances to weathering depths.

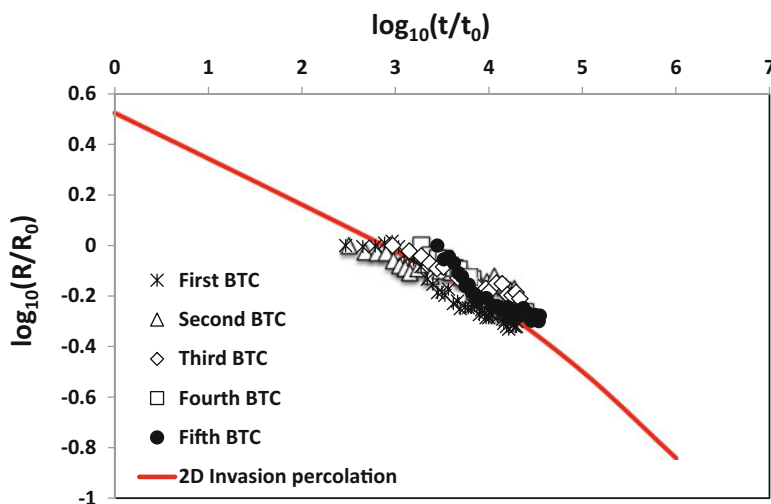
We consider the spatial data of Maher (2010) (Fig. 12) and the temporal data of White and Brantley (2003) (Fig. 10) together, since both of these curves are generated by the same set of system parameters and thus generate the same functional dependence of $\langle x \rangle$ on t . Further, we have assumed essentially the same flow rates and have calculated the fundamental time and length scales compatibly. Thus we see that the cross-over to a steeper decline in R that occurs between 1,000 and 10,000 years in Fig. 10 occurs at around the decimeter (ca. $300 \times 0.75 \text{ mm}$, the fundamental length scale of Maher 2010) length scale in Fig. 12. When length scales of 1–10 meters are reached (5 order of magnitude reduction in reaction rates), the time scale is a million years. This

indicates that typical (saturated) surface vertical flow rates controlled by gravity lead to solute transport distances of 1–10 m by about a million years, producing a weathering depth of meters after a million years. By the commonly observed equivalence between chemical weathering depths and physical denudation thicknesses (Dixon et al. 2009), weathering rates in meters per million years lead to similar denudation rates for weathering limited conditions, as obtained through cosmogenic and other methods of dating (Anderson and Anderson 2010). Accordingly, for conditions when chemical weathering rates govern soil loss, grain size transport distances at 1 s can be linked to common landscape surface losses on the order of meters to tens of meters over a time scale roughly equal to the geomorphic age, 5 Myr, of the earth's surface (Anderson and Anderson 2010).

Direct Comparison with Reactive Solute Transport Experiments

The following data sets were also addressed by Hunt et al. (2015). Now consider the dependence of uranium reaction rates on time scales from

various Hanford experiments. We start with data from Liu et al. (2008), because these authors give sufficient information for us to calculate t_0 , even if we cannot determine R_0 unambiguously. Their data were collected from both a short and a long column, but the medium characteristics were the same for both, and the sediments involved were very coarse. The flow rates differed substantially, however. The process for calculating t_0 involves conversion of a column-scale fluid velocity to a pore-scale fluid velocity, v , and then finding the ratio of a typical pore size to v_0 . We found a geometric mean particle size (excluding the gravel fraction of the soil) and assumed that the associated pore size was a factor 0.3 smaller (Gvirtzman and Roberts 1991). We could generate absolute time scales for both the short column and the long column experiments that are shown in Figs. 13 and 14 and establish that neither experiment was continued to times long enough to reach the predicted slope change. In order to plot all breakthrough curves for the same experimental apparatus on the same graph, we took the ratio of the concentration (assumed proportional to the reaction rate R) to its largest value and the ratio of



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 13 Comparison of theoretical solute velocity as a function of time with Uranium desorption data from the short column described by Liu et al. (2008). The various breakthrough curves were all normalized according to their

initial times and concentrations. This set of data is the only one analyzed here that is described by 2D invasion percolation exponents, implying that in this case flow was concentrated along the walls of the column under unsaturated conditions

t to its smallest value in each experiment. Then the logarithm of the ratio of the earliest arrival time to the calculated t_0 defines the onset of the data. The values of t_0 were 0.08 min for the short column, and 0.19 min for the long column. To generate the exact correspondences, we had to adjust a single constant in each graph, the value of R_0 . We used again $D = 2.95$. Notice that t_0 for the short column is 4.8 s, approximately half the fundamental time scale obtained for the fresh Panola plagioclase experiment of White and Brantley (2003).

The short column from Liu et al. (2008) (Fig. 13) is consistent with predictions from two-dimensional invasion percolation, indicating that the relevant portion of the medium is not saturated. In very coarse Hanford sediments it is known that flow along the wall of a sediment core can dominate due to the particularly large pore spaces formed along the boundary between the sediment and the wall (Cherrey et al. 2003). We were able (Ghanbarian-Alavijeh et al. 2012) to predict the entire solute arrival time distribution (Cherrey et al. 2003) using two-dimensional values of relevant percolation exponents and system parameters extracted from pressure-saturation curves. The interpretation is based on the fact that, for coarse soils, very large pores can be found at the wall of the core. But it may be difficult to force 100% saturation of these pores. If they form only 5% of the pore space, even if they are only 80%

saturated, the system saturation will be 99%, which is difficult to distinguish from 100%.

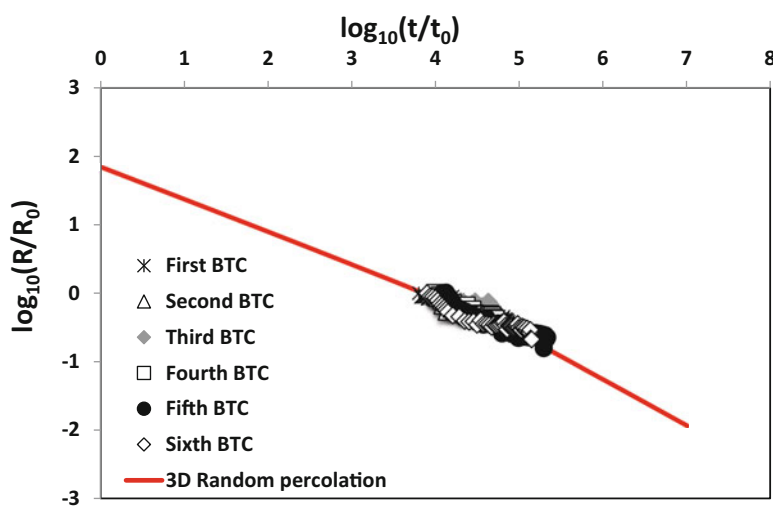
The long column from Liu et al. (2008) (Fig. 14) is consistent with predictions from three-dimensional random percolation, indicating that the entire medium was saturated.

Figure 15 shows software generated fits to the data in Figs. 13 and 14 and demonstrates that the exponents extracted by regression, 0.17 and 0.46, are almost identical to the theoretical values listed in Table 2 which are 0.18 for 2D invasion and 0.47 for 3D random percolation.

An interesting dependence of Uranium (VI) desorption concentrations on time was obtained by Liu et al. (2009). We digitized the data from Figs. 1 and 2 of that work. The time span was much shorter than the data summarized by White and Brantley (2003), however, covering only minutes to hours. This data sequence appears to show (Fig. 16) the same kind of cross-over to a steeper slope as seen in White and Brantley's (2003) data. This is generally consistent with the value of the controlling rate constant, $10^{-4.29}$, taken from Table 1 of Liu et al. (2009), which is five to six orders of magnitude greater than the largest lab values reported by White and Brantley (2003). Consequently, experimental conditions with much greater fluid velocities would still allow for transport-limited reaction rates. We accordingly

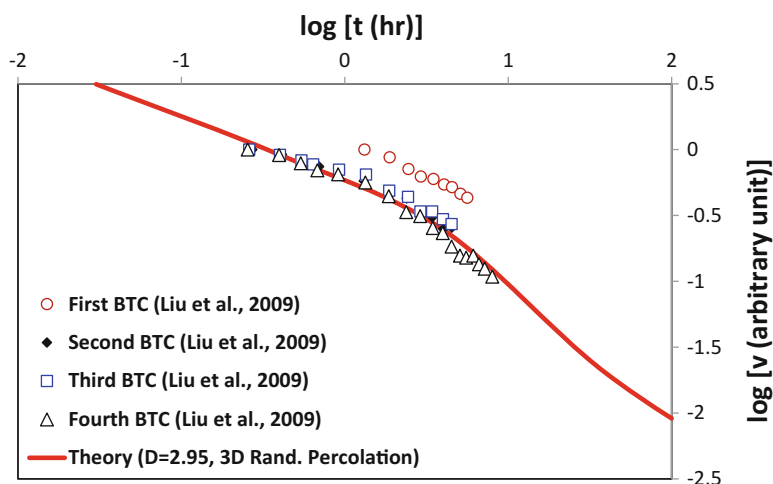
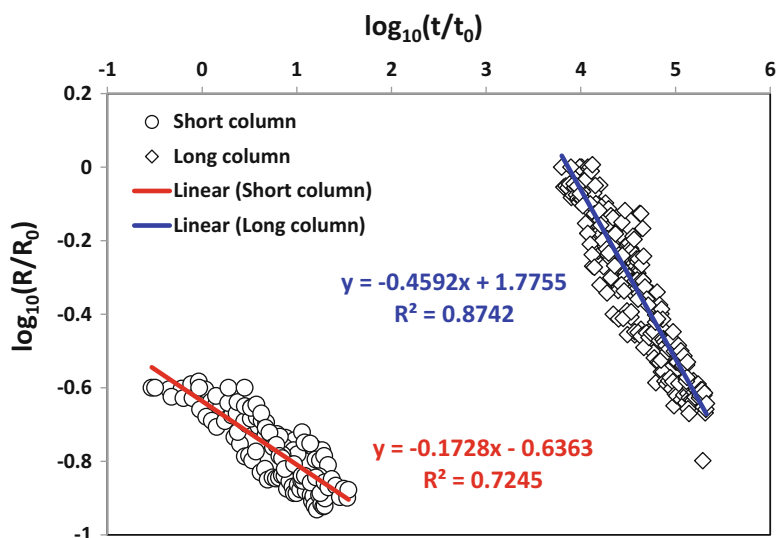
Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock,

Fig. 14 Comparison of theoretical solute velocity as a function of time with uranium desorption data from the long column described by Liu et al. (2008). The various concentrations were all normalized according to their initial times and concentrations. Here the usual random percolation exponents for 3D flow were applied



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Fig. 15 The same data are presented as in Figs. 13 and 14, but this time the exponents, 0.17 and 0.46, were determined by regression. These values are essentially equal to the values obtained from the theory tabulated in Table 2 for temporal scaling of the velocity, 0.18 and 0.47, for 2D invasion and 3D random percolation, respectively



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Fig. 16 Comparison of the theoretical solute velocity as a function of time with Uranium desorption data (Liu et al. 2009). The procedure for the experiment is described in

detail in Liu et al. (2009); the various breakthrough curves, however, correspond to renewed elution after hiatuses from stopped flow. We note that the displayed agreement between theoretical and experimental slope changes is possible only if the time scale chosen for theory is correct

changed the time axis scale from Fig. 10 by a factor of about 10^5 , and plotted the observed uranium concentrations as a function of time (Fig. 16). Reference to Fig. 10 shows that the individual weathering rate results cover only the initial and final slopes and do not show the actual behavior at the predicted slope crossover. But the uranium experiments shown in Fig. 16 appear to show the slope crossover.

We again used 3D random percolation exponents and the same medium model, $D = 2.95$.

Next consider data for uranium elution from Du et al. (2012). These authors report for experiments on uranium dissolution a dependence of uranium concentration that diminishes according to a power of the transport time. The data were collected from elution experiments for five different media with differing particle sizes. The

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Table 3 Calculated flow characteristics from the Du et al. (2012) experiment

Diameter, μm			Number of particles in 0.5 g	Mean distance between particles, μm	Flow time between particles, s	Column crossing time, h
Lower bound	Upper bound	Geometric mean				
20	75	38.7	6,202,812	117	28	177 (93)
75	500	193.6	49,622	586	141	43.8 (68)
500	2000	1000.0	360	3028	727	10.5 (34)
20	2000	200.0	45,044	606	145	42.3
2000	4000	2828.4	16	8563	2550	5.2 ^a

^aFor comparison in Fig. 17, 5.2 h was used for both runs

experiment was performed in a stirred “flow cell” 25 mm tall with 0.5 g of particles in 10 ml of liquid – in other words it was a suspension, not a grain-supported medium.

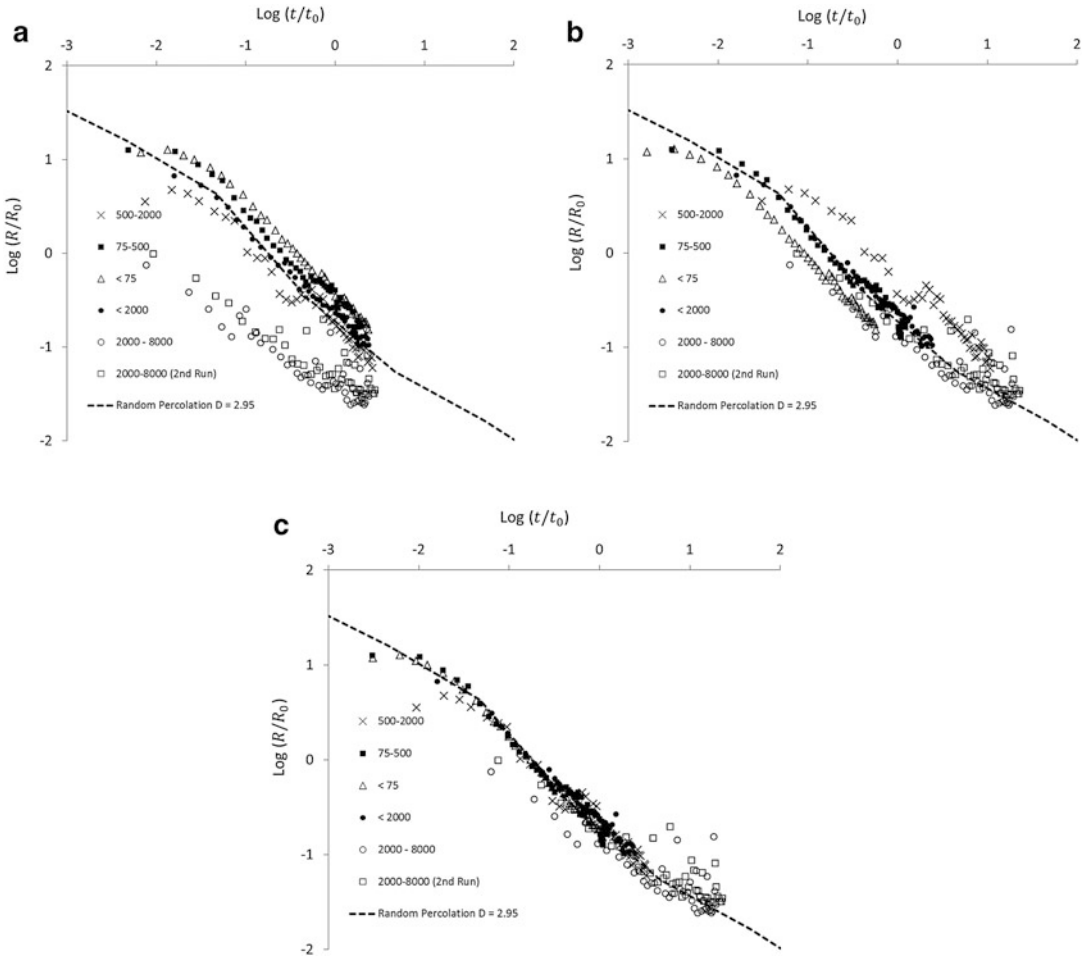
In Table 3 we use the published particle sizes and the particle numbers derived therefrom to calculate mean particle separations and the flow time (neglecting effects of stirring). The mean distance between the particles was calculated by assuming the particles were equidistantly dispersed. The total flow time was calculated from the product of an interparticle flow time with the 1.87 power of the quotient of the column length with the interparticle distance.

Results from two different runs of the experiment on the largest particles were compared (not shown). In order to generate the same regression coefficients in both experimental results, the time scale of the second run had to be chosen a factor 1.86 larger than for the first run, leading to the conclusion that the flow rates generally were probably not identical, but carried an uncertainty of about a factor 2. This provides a justification for choosing time scales somewhat different from those calculated in half of the experiments (the numbers in parentheses in Table 3, column 7).

The temporal dependence of the uranium concentration is compared with theory in the three panels of Fig. 17. In Fig. 17a we present the raw data from the experiments (with the exception that a linear relationship between pore volume and time has been assumed). Otherwise, we have made no changes. In Fig. 17b we present the data scaled to the predicted typical solute transport time (Table 3) through the column (calculation

method described below). In Fig. 17c we use knowledge that the run-to-run variability in the flow rate is about a factor 2 to adjust the time scales of each individual data set to fall on the same curve. We made no adjustments in the solute concentration, and altered assumed time scales in two cases by a factor of roughly 2, and a factor of roughly 3 in the third case.

Owing to the fact that the interparticle fluids were stirred, Du et al. (2012) interpreted their scale-dependence in terms of diffusion-limited transport within the particles. This interpretation is in accord with the understanding of Noniel et al. (2012), whose stirred experiments did not show evidence of transport-limited behavior at larger length scales. However, these interpretations do not consider the effects of tortuosity in the fluid paths. By tortuosity, we mean the ratio of the total path length between two points to the length of the vector displacement between the two points. Tortuosity is thus a measure of the increase in path length due to frequent changes in direction. We suggest that the time dependence of the solute transport over lengths equivalent to thousands of particle separations (as in the case of the smallest particles) is likely not reflecting the dynamics of the transport within the particles, but rather, the tortuosity of the paths through the porous medium as a whole. Furthermore, our solute velocity function in Fig. 17 is identical to that used in all the other figures, specifically that of Fig. 12, although in that case it is represented as a function of distance x , rather than of time, t . Consequently, the three spatial data sets from Fig. 12 could be mapped to precisely the function shown in Fig. 17



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 17 Comparison of the theoretical solute velocity as a function of time with elution data of Du et al. (2012). The different data sequences are for media with different particle sizes. We again used 3D random percolation exponents, consistent with three-dimensional flow and saturated

conditions, as well as the choice $D = 2.95$. In Figure (a), the data are plotted with unmodified time scales. In Figure (b) the fundamental time scales are adjusted as calculated in Table 3. In Figure (c) the time scales of the data are adjusted to collapse all the data onto the same curve and the values used are compared in Table 3 with those calculated

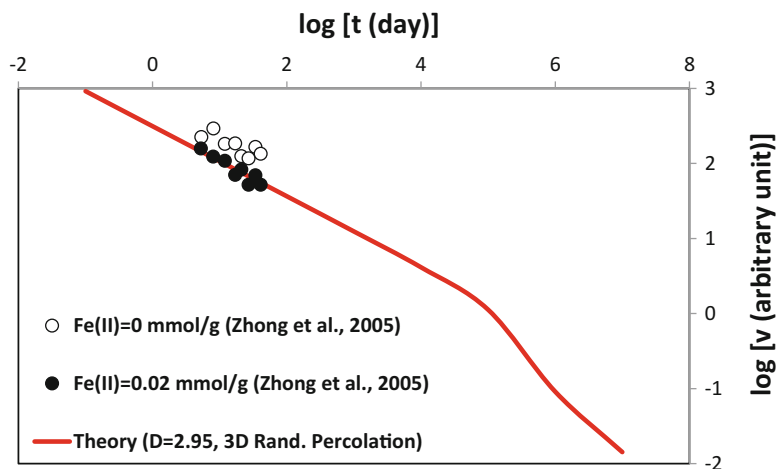
(as well as in the comparison with White and Brantley (2003)) allowing presentation of another three data sets that fit along the same curve.

Zhong et al. (2005) obtain a remobilization rate that decays as $t^{-0.53}$ (with $R^2 = 0.89$) or $t^{-0.42}$ (with $R^2 = 0.61$). Such a dependence on time would be in accord with either diffusion as a limiting mechanism, or with our results for transport-limited reaction rates. We compare their remobilization rate with our solute velocity predictions in Fig. 18 and find reasonably good

agreement. We again used 3D random percolation with the same medium characteristics, that is, $D = 2.95$.

Deep Tropical Weathering: Laterites, Bauxites, and Saprolites

In humid continental conditions where erosion rates are very small, climatic conditions may remain very similar for tens of millions of years – in one case even 150 Myr. In these cases, weathered depths may reach 100 m. Eq. (7) for the



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 18 Comparison of the theoretical solute velocity as a function of time with iron concentrations from Fig. 1b of Zhong et al. (2005). Data from other figures in this

reference could not be used since, in most cases, the iron concentrations did not exhibit a systematic behavior, but, rather fluctuated around a single value, or increased steadily with time

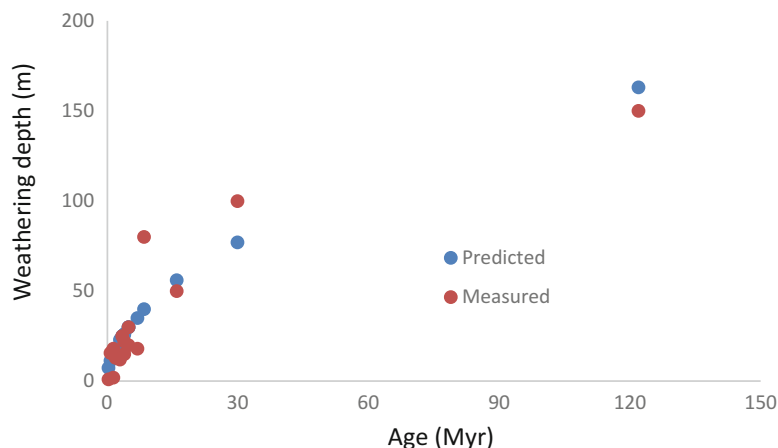
velocity of the weathering front may be integrated in time to generate the depth of the weathering front. This is a simple power law, $x = x_0 (t/t_0)^{0.53}$, with two unknown parameters, a length scale and a time scale. In order to generate a prediction for a typical depth at such enormous time scales, Yu and Hunt (2017a) took a typical median particle size in the middle of the silt range, 30 μm , for x_0 , and a typical yearly vertical flow rate of 0.5 m year^{-1} for x_0/t_0 , generating t_0 somewhat less than 2000 s. The yearly flow rate is derived from Lvovitch's (1973) estimates of precipitation, just under 1 m, and the fraction which actually infiltrates ca. 22%, divided by a typical porosity of about 0.4. While humid tropical and continental climates typically will have a higher precipitation than just 1 m, Eq. (7) neglects any change to a slower reaction rate at longer time scales. Figure 19 shows the success of that prediction.

Discussion

Clearly, our theoretical derivation omits factors that can have impacts on weathering rates, such as the pH of the fluid, precipitation of secondary minerals, surface roughness, temperature, porosity, and saturation conditions. But the predominant variability in experiment that we found relates to

conditions of saturation and of flow, for example, whether it is connected two-dimensionally or three-dimensionally. Weathering rind development on surface clasts in Alpine environments (Chinn 1981; Colman and Pierce 1986; Knuepfer 1994) (Table 2) was compatible with 2D flow under unsaturated conditions, while in humid, particularly tropical, environments (Fig. 3), it was compatible with 3D flow under unsaturated conditions. Submarine basalt weathering rind thicknesses increased (Moore 1966) according to the exponent appropriate for 3D flow under saturated conditions. All the weathering data compiled in White and Brantley (2003) and Maher (2010) as well as all experiments except one were compatible with 3D flow under saturated conditions.

Significantly, we find that the time and length dependences of reaction rates differ. Maher (2010), on the other hand, ascribes significance to her analyses showing nearly the same reaction rate dependences on both time and distance, at least in what is there denoted as the transport-limited regime. If these two dependences were the same, this would imply scale-independent solute velocities. But if these velocities are scale independent, then transport-limited reaction rates would also be scale-independent. Our analyses of



Application of Percolation Theory to Reaction and Flow in Geochemical Systems in Soil and Rock, Fig. 19 Comparison of simple scaling prediction for the weathering front depth as a function of time for times greater than 1 Myr (up to 150 Myr) with field results for “saprolites,” “laterites,” and “bauxites.” Parameter values typical of the world’s present soils and climates are used, as

described in the text, while the data sources are Wright (1994), Cooper (1936), Hill et al. (2000), Taylor et al. (1992), Boulange and Carvalho (1989), Freyssinet and Farah (1997), Pavich (1986), Bestland et al. (1996), and Migon and Lidmar-Bergstro (2002), Price et al. (2005), Cleaves et al. (1974), Pavich et al. (1989), Pavich (1989), and Felix-Henningsen (2018)

multiple data sets to determine the temporal and spatial dependences of the reaction rates show that these two different representations of the data exhibit distinct functional dependences, as expected from our theoretical development.

Our theory, in which transport limitations are from advection, generates reaction rates proportional to the fluid velocity, as was observed both in natural settings (Maher 2010) and in the laboratory (Salehikhoo et al. 2013). We find it significant that our theory generates scaling that is very nearly identical to diffusion for 3D random percolation (saturated conditions), and that behavior which mimics diffusion can be observed in both weathering rind development (Moore 1966) and weathering experiments (White and Brantley 2003). This coincidence reduces the motivation for assuming diffusion as the transport limitation and increases the basis for considering advection.

In our discussion we have assumed that variability in the value of D_b was restricted to four discrete values defined by random and invasion percolation theory in 2D and 3D. It is known that some percolation models with long range correlations in the permeability field can generate additional variability in D_b values (Sahimi 2012).

Whether other values will be relevant in real experiments cannot be stated at this time. The uncertainty in experimental time scales is, at this point, probably too large to make such an evaluation. However, the data from the experiments treated suggest that the D_b values used to construct Table 1 may be sufficient.

Finally, we consider the potential relevance of our calculations based on transport limitations to weathering in extreme environments. We quote Maher (2010): “Systems with surprising degrees of chemical weathering include deep-sea sediments (Maher et al. 2004, 2006a, b; Wallmann et al. 2008), saprolites (White et al. 2001; Price et al. 2005), and aquifers (Zhu 2005). The alternative driving forces in these systems, which may be partly to entirely dominated by diffusive transport, are: 1) the precipitation of secondary minerals (Maher et al. 2006a, b, 2009; White et al. 2009); and 2) the capacity of microbial activity to sustain departures from equilibrium via reaction networks (Maher et al. 2006a, b; Wallmann et al. 2008; Aloisi et al. 2004).” Note that data from Maher et al. (2004), Price et al. (2005), and Wallmann et al. (2008) could be included in the above analysis without apparent

deviations from our predictions. Thus our theoretical formulation appears to account for weathering in these extreme environments.

Conclusions

We tested our percolation-theoretical model of solute transport on a large number of different observations of chemical reaction rates in porous media. The framework for the calculations consisted of two simple, interrelated, hypotheses (i) that chemical weathering rates are limited by solute transport velocities (as calculated in percolation theory), and (ii) that solute transport distances control the depth of the surface weathered layer through the advance of the weathering front. Known results from percolation theory for the dependence of cluster surface area on cluster radius generated, using one adjustable parameter, the dependence of weathering rates (due to changing surface area) on measurement scale (Navarre-Sitchler et al. 2007). In predicting temporal or spatial weathering rate scaling for each data set, we applied the same characteristics of the medium, for example, porosity, critical volume fraction for percolation, and pore size distribution. But for some media, notably surface clasts, unsaturated, rather than saturated, conditions had to be assumed. The results include length and time scale dependences of experimental reaction rates, as well as length and time dependences of weathering rates observed in the field and the temporal dependence of weathering rind thicknesses. An excellent match between theory and experiment was found in each case. The results are also generally compatible with the interpretation of the origin of the surface weathered layer and its time scale for production and removal (Dixon et al. 2009) under conditions of weathering rate control. Our theory of solute transport is well established for conservative solute transport (Hunt and Skinner 2008, 2010a, b; Hunt et al. 2011; Ghanbarian-Alavijeh et al. 2012), but this current study is among the first investigations of its potential relevance for reactive solute transport.

The much thinner weathered crusts on surface clasts are a product of their relatively small hydraulic conductivity when compared with unconsolidated porous media and fractured bedrock, from which soils form through chemical weathering much more easily.

Our results suggest that the perceived complexity of reactive solute transport can be related to known behavior of nonreactive solute transport if one uses concepts from percolation theory as the basis for the theoretical calculations and solute velocities as a proxy for reaction rates.

Other related topics that have been addressed include the relationship between soil production and chemical weathering, and the implications of these processes for past and future climate change. Eq. (11) can be utilized for calculating steady-state soil depths, when soil erosion and soil production rates are equal, if the soil erosion rate is known (Yu et al. 2017, 2019), while Eq. (7) can be applied when erosion rates are negligible. Jenny (1941) presented as a hypothesis the existence of a soil formation function of five variables, climate (cl), organisms (o), relief (r), parent material (p), and time (t). Yu et al. (2017, 2019) and Yu and Hunt (2017a) show that such a hypothesis is satisfied using the framework of Eqs. (7) and (11) here, and that the theoretical dependence on each variable ($clorpt$) is in accord with experiment. Here cl enters in the flow rate, t is explicit, r enters in the erosion rate as a function of slope angle, p is the particle size, and organisms enter in both the flow rate (precipitation less transpiration through the plants) and the form of the equation, based on chemical weathering limitations from transport. Without the acids produced by metabolism and decay of plants, the chemical weathering would not be a factor in the soil development.

Productivity of ecosystems and water accessed by plants both depend sensitively on soil depth, adding further related topics of significance.

Future Directions

As of this time, no comprehensive theoretical approach exists that can accurately predict the regime of mixed kinetics and transport controls

as well as the long-term asymptotic transport-limited regime. The mixed regime is often handled within the traditional framework of partial differential equations. It is difficult to address the mixed regime and the asymptotic transport-limited regime simultaneously because the underlying physics at the two widely differing time scales is so different. This is a topic that warrants considerable future investigation.

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Application of Percolation Theory to Statistical Topographies

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Article Outline

Introduction
Relevant Contribution of Spatial Correlations
Characteristic Features of Earth's Topography
Geometrical Phase Transition on the
Experimentally Grown Surfaces
Percolation Theory and Earth's Topography
Critical Nodes in Earth's Relief Network
Future Directions
Bibliography

Keywords

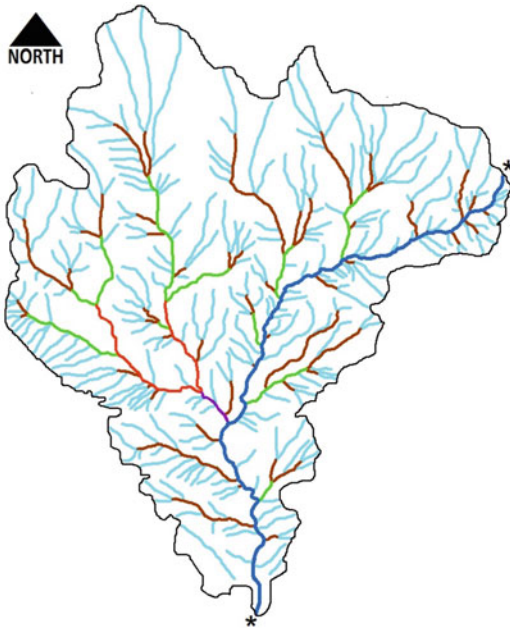
Percolation transition · Statistical topography ·
Earth's landscape · Iso-height lines

Introduction

Percolation theory (Saberi 2015) provides a suitable platform to study the properties of real and artificial landscapes (Isichenko 1992). A landscape is a height profile $\{h(x)\}$, usually defined on a square lattice where each cell's elevation value at position $x = (x, y)$ represents the average elevation over the entire footprint of the cell (site). Now imagine that the water is dripping uniformly over the landscape and fills it from the valleys to the mountains, letting the water flow out through the open boundaries. During the raining, watershed lines may also form which divide the landscape into different drainage basins – see Fig. 1.

Watersheds play a fundamental role in geomorphology in, e.g., water management (Vorosmarty et al. 1998) and landslide and flood prevention (Lee and Lin 2006). For a given landscape represented as a digital elevation map (DEM), it is possible to determine the watershed lines based on the iterative application of invasion percolation (Fehr et al. 2009). It is found (Fehr et al. 2012) that the main watershed line generated on random uncorrelated landscapes are self-similar with fractal dimension $d_f = 1.2168 \pm 0.0005$. It has been also shown that a watershed line is statistically compatible with the family of conformally invariant stochastic Loewner evolution (SLE κ) curves with $\kappa = 1.734 \pm 0.005$ (Daryaei et al. 2012). Watersheds and the shortest paths on critical percolation clusters with $\kappa = 1.04 \pm 0.02$ (Posé et al. 2014) are examples of unusual universality classes. Watersheds can also be defined in higher dimensions (Schrenk et al. 2012a).

By raising the water level through the landscape, different lakes gradually form and start merging with each other to form larger and larger lakes. It is reasonable to expect that at a certain water level, a percolation transition of the lakes would happen to form a giant lake so that it touches the borders and the water can indeed flow out of the landscape. This problem is closely related to the retention capacity of the landscapes addressed in (Baek and Kim 2012; Schrenk et al. 2014; Knecht et al. 2012). Whether the percolation transition is critical or not is strongly dependent on the spatial behavior of the correlations between the height variables (Schmittbuhl et al. 1993). For self-affine surfaces with positive Hurst exponent H (Sahimi 1994a, 1995, 1998; Sahimi and Mukhopadhyay 1996; Knackstedt et al. 2000) where the correlation behaves like $\sim(1 - r^{2H})$ with the spatial distance r , there will not be a genuine percolation transition, while for a long-range correlated surface in which the correlation decays with the distance as $\sim r^{-2H}$ with $H > 0$, the percolation transition is critical (Saberi 2010) and corresponding critical exponents change with H (Sandler et al. 2004;



Application of Percolation Theory to Statistical Topographies, Fig. 1 Fractal structure of a natural watershed at the north of Tehran, Darabad. The main watershed is the (blue) curve connecting the two points marked by ★

Schrenk et al. 2013; Weinrib and Halperin 1983; Janke and Weigel 2004). The fractal dimension of the watersheds (Fehr et al. 2011a, 2012) as well as various geometric features is dependent on H (Kondev and Henley 1995; Kondev et al. 2000; Schwartz 2001; Mandre and Kalda 2011). It has been verified numerically that the duality relation, as a characteristic property of conformally invariant fractals (Duplantier 2000), also holds for the perimeter of the largest cluster in the full range of Hurst exponents (Schrenk et al. 2013; Schrenk 2014).

For real landscapes, for example, percolation theory provides an interesting description for the global topography of Earth. It is found in Saberi (2013) that a percolation transition occurs on Earth's topography in which the present mean sea level is automatically singled out as a critical level in the model. This finding elucidates the origins of the appearance of ubiquitous scaling relations observed in the various terrestrial features on Earth. This transition is shown to be accompanied by a continental aggregation

which sheds light on the possibility of the important role played by water during the long-range topographic evolutions. The criticality of the current sea level also justifies the appearance of the scale (and conformal) invariant features on Earth, e.g., the fractal rocky coastlines (Boffetta et al. 2008), with an intriguing coincidence of the dominant $\sim 4/3$ fractal dimension in the critical model. The geometrical irregularity of the shorelines actually helps damping the sea waves and decreasing the average wave amplitude. A simple model is accordingly presented in Sapoval et al. (2004), which produces a stationary artificial shoreline related to the percolation geometry. A practical application for the discovery of the conformal invariance in the statistical properties of the shorelines is that it allows one to analytically predict the highly intermittent spatial distribution of the flux of pollutant diffusing ashore (Boffetta et al. 2008). The statistical properties and the modeling of the seashores and watersheds will be outlined shortly in the following. We explain how percolation theory can describe the origins of the appearance of various fractal patterns on Earth which can be applied to other planets as well. Since the statistical properties of different landscapes are highly dependent on the type of correlations existing in the height profile, let us shortly address how spatial correlations act when gradually introduced in a given height sample ranging from short-range to long-range contribution.

Relevant Contribution of Spatial Correlations

In the standard percolation models, all random occupations are considered to be independent of each other with no spatial correlations. But this is not always the case when, for instance, percolation theory is applied to study transport and geometric properties of disordered systems (Du et al. 1995; Coniglio et al. 1979; Makse et al. 1995, 1998, 2000; Araújo et al. 2001, 2003), or the properties of real and artificial landscapes discussed in the previous section “Introduction,” since the presence of disorder

usually introduces spatial correlations in the model. For sufficiently short-range correlations, the properties of the model will be the same as those of uncorrelated percolation. By increasing the range of correlations however, they may have a relevant contribution leading to new fixed points in the renormalization group study of the model. These can be quantified in terms of how the correlation function $g(r)$ falls off at large distances r : When the correlations are short-range with a fall-off faster than r^{-d} , then according to the Harris criterion (Harris 1974), they are relevant if $d\nu - 2 < 0$, where ν is the correlation length exponent for the uncorrelated percolation model. Since for the percolation model we always have the hyperscaling relation $d\nu - 2 = -\alpha > 0$, short-range correlations do not change the critical behavior (Weinrib and Halperin 1983). For long-range correlations of the power-law form $g(r) \sim r^{-2H}$ with $2H < d$ instead, the extended Harris criterion (Weinrib 1984) states that the correlations are relevant if $H\nu - 1 < 0$. In this case, the new correlation length exponent is given by the scaling relation $\nu_H = 1/H$. This relation has been then verified numerically in (Saber 2010; Makse et al. 2000; Marinov and Lebowitz 2006; Prakash et al. 1992; Abete et al. 2004). Thus the critical exponents in a long-range *correlated percolation* can change depending on how the correlations decay with the spatial distance.

Such a power-law decay of the spatial correlations is a typical characteristic feature of the height profile $\{h(x)\}$ in random grown surfaces. This indeed provides a convenient way to tackle with the correlated percolation on a lattice. For self-affine surfaces for which $g(r) \sim (1 - r^{2H})$, it is shown in Schmittbuhl et al. (1993) that even in the thermodynamic limit, the percolation transition is only critical for $H = 0$. Percolation on these surfaces is actually governed by the largest wavelength of the height distribution, and thus the self-averaging breaks down. For long-range correlated surfaces where $g(r) \sim r^{-2H}$, in contrast, the transition is critical and the self-averaging is recovered. Depending on the value of H , the correlation-length exponent is given as follows

$$\nu_H = \begin{cases} 1/H & \text{if } 0 < H < 1/\nu, \\ \nu & \text{if } H \geq 1/\nu, \end{cases} \quad (1)$$

where $\nu = 4/3$ for a Euclidean lattice in 2D. It is thus natural to expect that other critical exponents also depend on H . Such a dependence is numerically verified for the fractal dimensions of the largest cluster d_{fH}^c , its perimeter d_{fH}^P and external perimeter d_{fH}^{EP} , shortest path, backbone, and red sites (Schrenk 2014). It has also been shown that, within the numerical accuracy, the hyperscaling relation $d = (\gamma_H + 2\beta_H)/\nu_H = \gamma_H/\nu_H + 2(d - d_{fH}^c)$ is fulfilled by the exponents. The duality relation $(d_{fH}^{EP} - 1)(d_{fH}^P - 1) = 1/4$ is numerically shown to be valid, though the theoretical verification of these observations is still lacking.

Characteristic Features of Earth's Topography

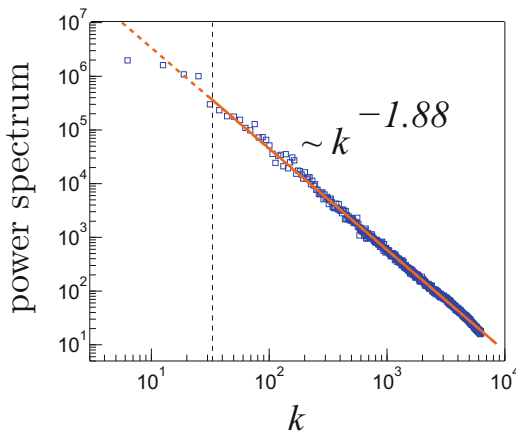
Percolation theory has been extensively applied to describe the properties of both artificial and natural landscapes. Percolation properties of the correlated surfaces as a model of wide range of artificial landscapes have been discussed in section “[Relevant Contribution of Spatial Correlations](#).” Our main focus in this section is mostly devoted to the statistical properties of natural landscapes and their modeling.

The power spectrum S of linear transects of Earth's topography has a remarkable characteristic scaling relation with the wave number k as $S(k) \sim k^{-\beta_c}$ with the exponent $\beta_c \simeq 2$, over a wide range of scales (Meinesz 1951; Mandelbrot 1975; Sayles and Thomas 1978; Newman and Turcotte 1990). (The power spectrum $S(k)$ is defined as the square of the coefficients in a Fourier series representation of the transect, which measures the average variation of the function at different wavelengths. For totally uncorrelated adjacent data points $S(k)$ is a constant, while for strongly correlated ones relative to points far apart, it will be large at small k (long wavelengths) and small at large k (short wavelengths).) Similar scaling relations have been

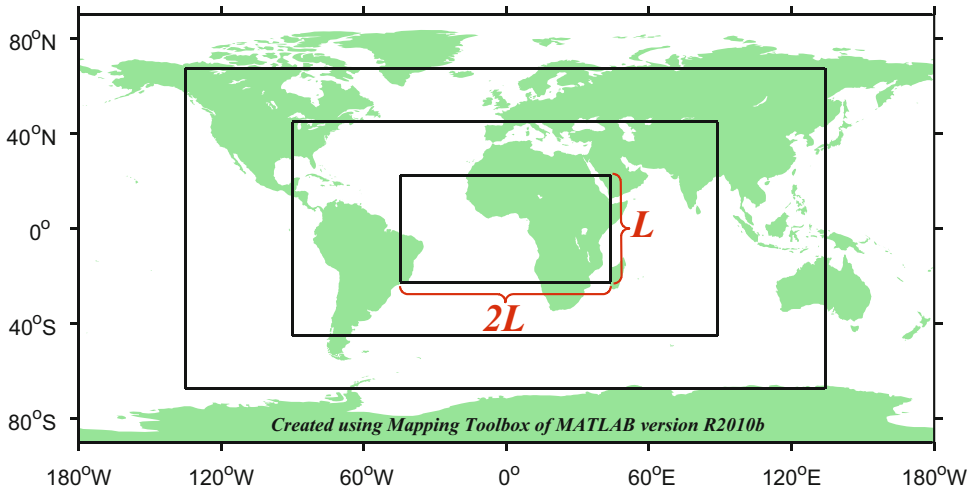
identified in Earth's bathymetry (i.e., the underwater equivalent to topography) (Bell 1975), the topography of natural rock surfaces (Brown and Scholz 1985), and the topography of Venus (Kucinskas et al. 1992). However, a more precise study on the spectral analysis of Earth's data (shown in Fig. 2) averaged over all latitudes have provided an updated value for the exponent $\beta_c = 1.88(10)$ (the numbers in the parenthesis show the uncertainty on the last digits). Further cross-check analysis also showed that this value is more reliable than the previous estimates (Fallah et al. 2016). Such a power-law spectrum in the topography is responsible for the appearance of various self-similar patterns on Earth, e.g., fractal coastlines (Mandelbrot 1967), the radiation fields of volcanoes (Harvey et al. 2002; Gaonac'h et al. 2003), crustal density and gravity (Pilkington and Todoeschuck 2004), geomagnetism (Pecknold et al. 2001), and surface hydrology such as in the river basin geomorphology (Rodriguez-Iturbe and Rinaldo 1997). Although environmental parameters such as erosion seem to play an important role in shaping the coastlines, drainage basins, and watersheds, the observation of scale-invariant topography on Venus, however, indicates that fractal

topography can be formed without erosion. The exponent β_c is related to the Hurst exponent H in fractional Brownian motion (fBm) via $\beta_c = 2H + 1$, thus suggesting $H \simeq 0.5$ for Earth's topography (for $\beta_c \simeq 2$). However, further surveys based on the fBm model (Mandelbrot 1975) of topography or bathymetry revealed a more complex multifractal structure of Earth's morphology giving rise to distinct scaling properties of oceans, continents, and continental margins described by $H = 0.46, 0.66$, and 0.77 , respectively (Gagnon et al. 2006). One can, however, reevaluate the Hurst exponent for Earth's topography by measuring the variance of the height profile within an ensemble of randomly chosen windows of size $2L \times L$ (Fig. 3) such that it covers the whole data set at the largest scale. Figure 4 shows the results of the power-law analysis for Earth's topography. Vertical dashed-line indicates an upper limit for the scaling region where the box is crossing a scale before which the boxes are randomly chosen on Earth's topography and the averages are taken over a relatively large number of samples. Above this scaling region, where the box size approaches the system size, the variance is just taken over the chosen box. Therefore, one concludes that the observed deviation from the scaling law in the latter region is due to the lack of appropriate ensemble averaging. The behavior can indeed be obtained by extrapolating the scaling behavior to the whole region outside the scaling region. Our discussed approach captures the scaling exponent $2H \sim 0.88$ in the global Earth's topography which is in good agreement with the previous estimate by the spectral analysis given by $(\beta_c - 1) \sim 0.88$ (Fallah et al. 2016).

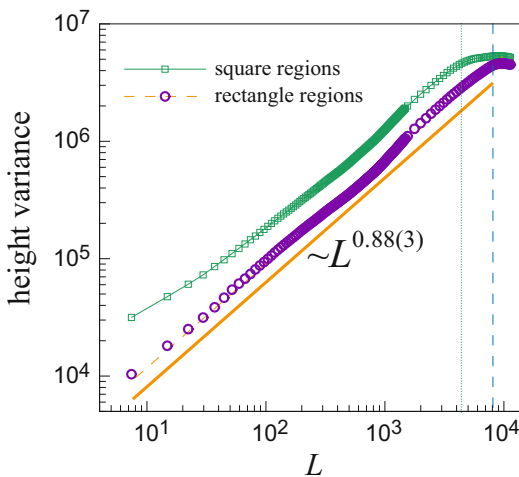
The other characteristic feature of Earth's topography is its bimodal distribution (Wegener 1966) which reflects the topographic dichotomy of continents and ocean basins. Remarkably, such bimodality has been recently observed (Saberi 2013; Fallah et al. 2016) for other quantities as well, for example, in the probability distribution function of the near-surface temperature and in the total length of the coastlines on Earth (Fig. 5). The bimodal topography has a clear discrepancy with Gaussian models of topography, also consistent with the Mandelbrot's observation (Mandelbrot



Application of Percolation Theory to Statistical Topographies, Fig. 2 The plot of the power spectrum $S(k)$ versus the wave-number k for the Earth's data. The solid line indicates the power-law fit to the data in the scaling region followed by the extrapolated dashed line for the large length scales



Application of Percolation Theory to Statistical Topographies, Fig. 3 Schematic of several boxes selected for the power-law analysis



Application of Percolation Theory to Statistical Topographies, Fig. 4 The plot of the height variances within the boxes that are randomly chosen on Earth topography (square symbols are for the square $L \times L$, and circle symbols are for the rectangle $(2L \times L)$ box sizes). The solid line shows the best power-law fit

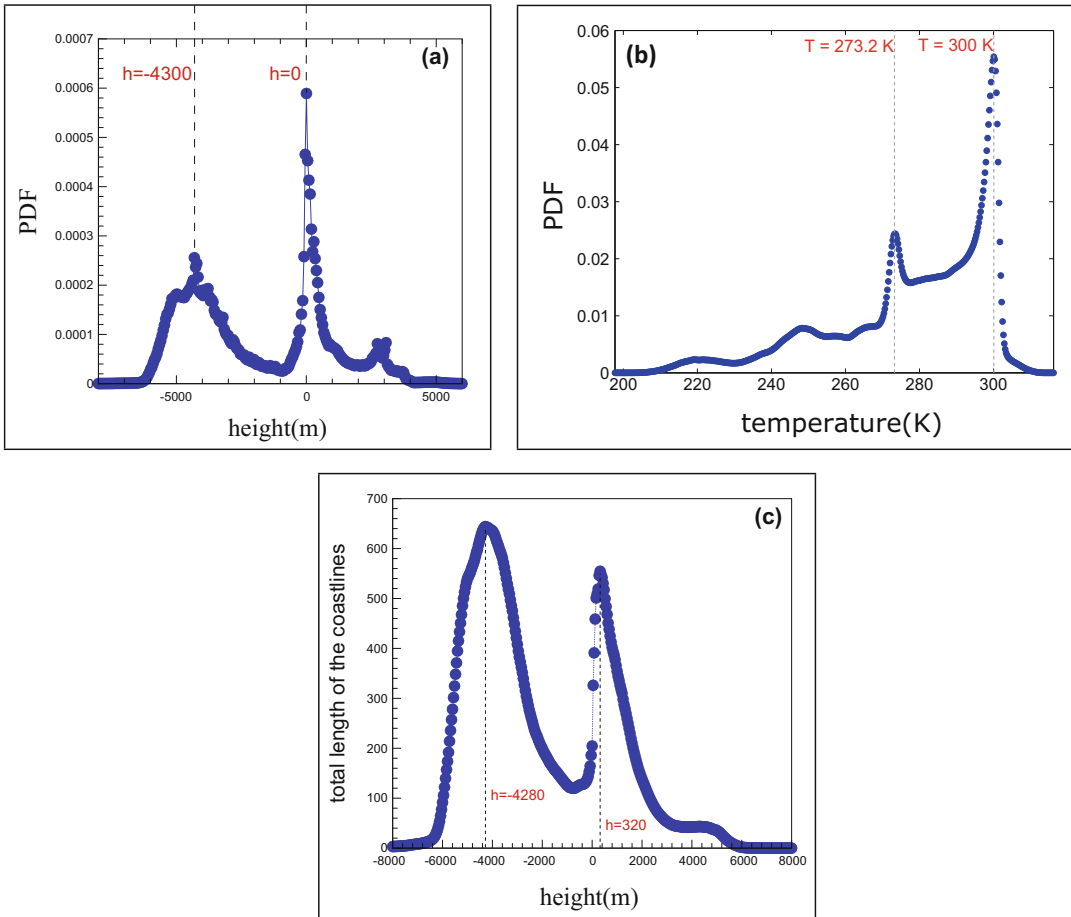
1983). The positive correlation between elevation and slope seen on Earth (i.e., the steepness increases with the height) is not also predicted by a model with a Gaussian distribution, implying that the global topography of Earth is not easily amenable to modeling.

Nevertheless, percolation theory has been recently applied to describe the global topography

of Earth (Saberi 2013; Fan et al. 2019), in which the critical point indicates the present mean sea level. Moreover, different models based on percolation theory have been proposed to describe the statistical properties of regional features on Earth such as coastlines (Sapoval et al. 2004; Morais et al. 2011), river basins and drainage networks (Maritan et al. 1996; Banavar et al. 1997; Cieplak et al. 1998; Colaioni et al. 1997; Hergarten and Neugebauer 2001; Stark 1991), and watersheds (Fehr et al. 2009, 2011a, 2012; Herrmann and Araújo 2011). Percolation theory has been also successful to help understand other phenomena on Earth. It has been demonstrated (Golden et al. 1998) that sea ice exhibits a percolation transition at a critical temperature above which brine carrying heat and nutrients can move through the ice, whereas for colder temperatures the ice is impermeable. Percolation also serves as an attractive mechanism to explain core formation in Earth (Shannon and Agee 1998; Mann et al. 2008).

Fractal Geometry of Coastlines

Coastlines were among the first natural systems that were quantitatively characterized when Mandelbrot computationally analyzed their fractal geometry (Mandelbrot 1967). In fact, the geometrical irregularity of the coastlines helps damping the sea waves and decreasing the



Application of Percolation Theory to Statistical Topographies, Fig. 5 Observation of bimodality in (a) probability distribution function (PDF) of Earth's

topography, (b) PDF of the near-surface temperature of Earth, and (c) total length of the coastlines on Earth

average wave amplitude. Affected by the sea eroding power, an irregular morphology evolves at the rocky coast until a self-stabilization with the wave amplitude is established. A simple model of such stabilization has been studied (Sapoval et al. 2004) in which the fractal geometry of the coastline plays the role of a morphological attractor directly related to percolation geometry. Dynamics of the model spontaneously leads to a stationary fractal geometry with a dimension very close to $4/3$ independent of the initial morphology, in agreement with that observed on real coasts (Mandelbrot 1967; Sapoval 1989). This fractal dimension is also consistent with that of the external perimeter of the spanning

cluster in a 2D critical percolation. Two general erosion mechanisms are considered in the 2D model, i.e., a rapid mechanical erosion and a slow chemical weakening. It has been shown that when the model involves both processes, a dynamic equilibrium is reached that changes the shape of the coast but preserves its fractal properties.

The effect of spatial long-range correlations in the lithology of coastal landscapes on the fractal properties of the coastlines has then been addressed in Morais et al. (2011). In fact, due to the *endogenic* processes like volcanic activity, earth-quakes, and tectonic processes originating within Earth that are mainly responsible for the

very long-wavelength topography of Earth's surface, one naturally expects that lithological properties of coastal landscapes would be in general heterogeneous as well as long-range correlated in space. Moreover, a multitude of fractal dimensions has been measured for real coastlines of different landscapes (Richardson 1961). Thus self-similar geometry of coastlines should emerge from an intricate interplay between these landscape properties and the sea force. The results of a simple invasion model (Moraes et al. 2011) indicate that a critical sea force f_c exists at which the coastline exhibits self-similarity with fractal dimension depending on Hurst exponent. The dominant $4/3$ fractal dimension was obtained for uncorrelated landscapes. For $f < f_c$ the coastline is rough but not fractal and the eroding process stops after some time, while for $f > f_c$ erosion is perpetual leading to a self-affine coastline which belongs to the Kardar-Parisi-Zhang (KPZ) (Kardar et al. 1986) universality class.

The external perimeter of critical percolation clusters with fractal dimension $4/3$ is proven to have a conformally invariant limit described by $\text{SLE}_{8/3}$ (Smirnov 2001; Bollobás and Riordan 2006; Sun 2011; Beffara 2008). Some numerical evidence of such a strong symmetry has been also reported for rocky coastlines with fractal dimension $4/3$ (Boffetta et al. 2008). These coastlines are therefore shown to be statistically equivalent to the external perimeter of percolation clusters or that of planar random walk. The conformal invariance can then be used to predict the statistics of the flux of pollutants diffusing over shorelines. This flux has been characterized by a strongly intermittent spatial distribution which can vary dramatically between locations just a few hundred meters apart.

Strong evidence of conformal invariance property has been also presented for the iso-height lines (like coastlines) of both artificial landscapes in the KPZ universality class (Saber et al. 2008a, 2010; Saber and Rouhani 2009) and experimentally grown surfaces (Saber et al. 2008b). In the KPZ universality class, the iso-height lines are characterized by a fractal dimension of $4/3$ with the same conformal invariant properties as the external perimeter of critical percolation clusters,

compatible with $\text{SLE}_{8/3}$ curves in the scaling limit. Such an analogy may lead to an alternative description of the coastlines.

Statistical Properties of Watersheds

The watershed is defined as the line which separates adjacent drainage basins – see Fig. 1. Based on observation of natural watersheds, it has been claimed that they should have a fractal structure (Breyer and Scott Snow 1992). The self-similarity of watersheds has then been justified numerically for both natural and artificial landscapes (Fehr et al. 2009, 2011a, b). Watersheds have been shown to be related to a family of curves appearing in different contexts, e.g., bridge percolation (Schrenk et al. 2012b), polymers in strongly disordered media (Porto et al. 1997), optimal path cracks (Andrade Jr. et al. 2009), and fracturing process (Moreira et al. 2012). To determine the watershed lines on real or artificial landscapes which are usually in the form of DEM, consisting of discretized elevation fields, one can use an iterative application of an invasion percolation procedure (Fehr et al. 2009).

The fractal dimensions of watershed lines in 2D and 3D were estimated (Fehr et al. 2012) to be $d_f = 1.2168 \pm 0.0005$ and 2.487 ± 0.003 , respectively, for uncorrelated artificial landscapes. In two dimensions, however, the measured fractal dimension for natural landscapes obtained from data provided by satellite imagery (Farr et al. 2007) falls into the range $1.10 \leq d_f \leq 1.15$. This may imply the necessity of considering spatial correlations in computations. When the long-range correlations characterized by the Hurst exponent H were introduced (Fehr et al. 2011b), a monotonic decrease of d_f with H has been observed, and the agreement with the observation achieved for $0.3 < H < 0.5$ (although this range of H seems to be out of that observed for continents and continental margins (Gagnon et al. 2006)). Moreover, it has been shown (Fehr et al. 2011a) that small and localized perturbations, such as landslides or tectonic activities can have a large and nonlocal impact on the shape of watersheds. It is also discussed in Herrmann and Araújo (2011) that the fractal dimension obtained in 2D for uncorrelated artificial landscapes is intriguingly

close to the fractal dimension of the largest cluster boundary in two models of explosive percolation on a lattice, i.e., the *largest cluster* and *Gaussian* models (Araújo and Herrmann 2010).

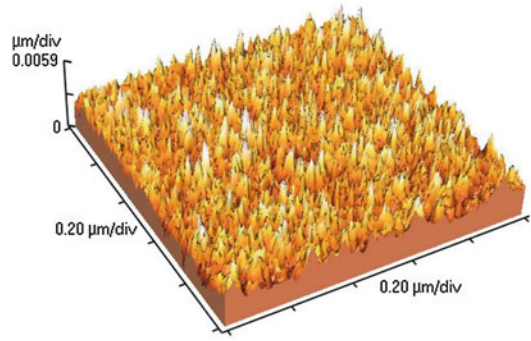
Watersheds are shown (Daryaei et al. 2012) to be among the rare examples of physical systems described by SLE_κ curves with $\kappa < 2$. It has been numerically shown that, in the scaling limit, the watershed line exhibits conformally invariant properties compatible with SLE_κ with $\kappa = 1.734 \pm 0.005$.

Geometrical Phase Transition on the Experimentally Grown Surfaces

The appearance of scale and conformal invariance property in statistical models such as percolation is a specific feature of criticality. This provides motivation for searching for an underlying mechanism that possibly explains the emergence of fractal geometries on various landscapes. For instance, it has been shown for an ensemble of experimentally grown WO_3 surfaces (Saber 2010) that there exists a critical level height at which a percolation transition occurs. This may elucidate the earlier observation (Saber et al. 2008b) of conformal invariant iso-height lines on these samples.

In order to see how percolation theory works for the ensemble of WO_3 surfaces, let us first define islands on a WO_3 surface. A cut is made at a certain height $h_\delta = \langle h(r) \rangle +$

$\delta \sqrt{\langle [h(r) - \langle h(r) \rangle]^2 \rangle} = 0$, where the symbol $\langle \dots \rangle$ denotes for spatial averaging. Each island (cluster-height) is then defined as a set of nearest-neighbor connected sites of positive height. One can then show that there is a critical level height denoted by the dimensionless parameter $\delta = \delta_c$, at which a continuous percolation transition occurs. To this aim, one can study the finite-size scaling (FSS) properties and measure percolation observables which characterize the critical behavior. A box of dynamic size $L \times L$ is considered from the centric region of each original atomic force



Application of Percolation Theory to Statistical Topographies, Fig. 6 AFM image of WO_3 thin film in scale $1 \mu m \times 1 \mu m$ with resolution of $1/256 \mu m$

microscopy (AFM) sample (Fig. 6), as we have shown before in Fig. 3. For each lattice size $16 \leq L \leq 256$, the percolation observable is averaged over all number of AFM samples.

Figure 7 shows the probability P_s that at each level height δ , a super large island spans two opposite boundaries of the box in just a specific direction, say y -direction. Ideally, the curves obtained for different lattice sizes cross at a single point, marking the critical level height δ_c . As shown in Fig. 7, the measured curves cross at $\delta = \delta_c$, implying that the scaling dimension of the percolation probability P_s is zero.

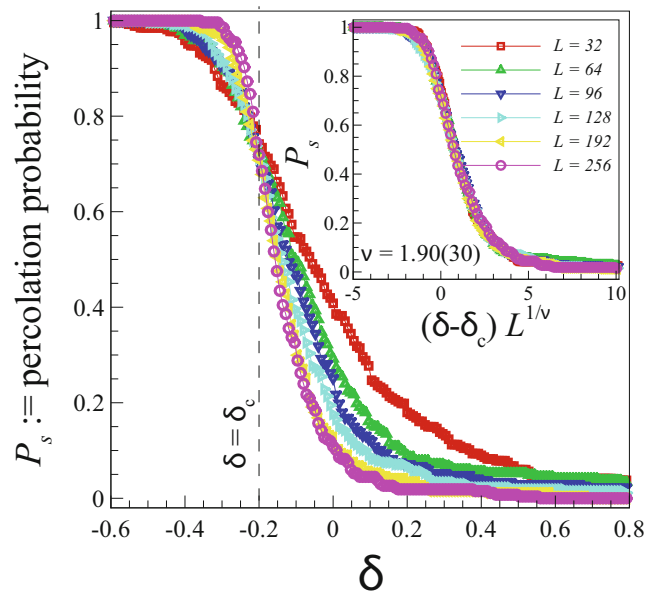
According to scaling theory (Binder and Heermann 1997), one expects that all the measured curves should obey the scaling form

$$P_s(\delta) = P_s \left[(\delta - \delta_c) L^{1/\nu} \right], \quad (2)$$

where the exponent ν characterizes the divergence of the correlation length ξ (proportional to the spatial extent of the islands) near the percolation threshold, i.e., $\xi \sim |\delta - \delta_c|^{-\nu}$. The values of the exponent ν and the crossing point of the curves δ_c can be measured by utilizing the data collapse. The quality of the collapse of the curves is measured by defining a function $S(\nu, \delta)$ of the chosen values ν and δ (the smaller S is indicative of a better quality of the collapse – see (Kawashima and Ito 1993; Bhattacharjee and Seno 2001) and the appendix of Houdayer and Hartmann (2004)). One can find its minimum $S_{\min} \sim 1.78$ for

Application of Percolation Theory to Statistical Topographies,

Fig. 7 Main: probability P_s for the presence of a spanning island as a function of δ measured for different lattice sizes L on an ensemble of experimentally grown WO_3 surfaces. The curves cross at a critical level height $\delta_c = -0.20(1)$. Inset: data collapse for the P_s curves of different L with the correlation length exponent $\nu = 1.90$ and $\delta_c = -0.20$



$\nu = 1.90(30)$ and $\delta_c = -0.20(1)$. Inset of Fig. 7 illustrates the collapse of all the P_s curves, within the achieved accuracy, onto a universal function by using the estimated values for ν and δ_c . The full set of percolation exponents can be accordingly measured (Saber [2010](#)) by computing various observables which show that the surface belongs to the long-range percolation universality class.

Percolation Theory and Earth's Topography

The ubiquitous scale invariant features on Earth have endowed theoretical interest on the assumption that they may reveal prevalence of some underlying feature (Bak [1996](#); Jensen [1998](#); Sornette [2000](#)). This is still an open question if there exists a clear relationship between the quantitative properties of landscapes and the dominant geomorphologic processes that originate them. Although such a relationship is established for some of the regional features, the global topography in comparison, has received less attention.

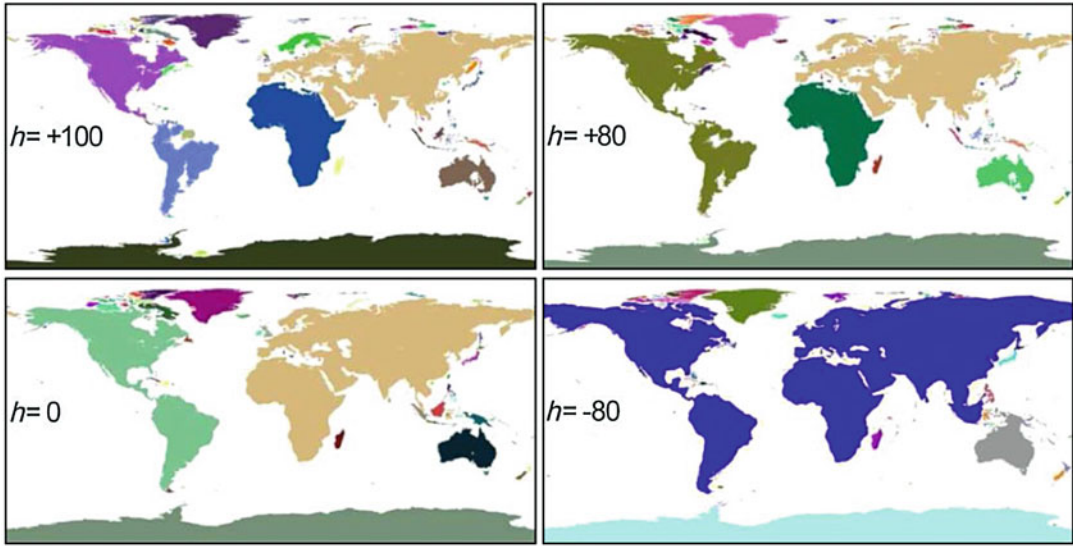
A percolation description of the global topography of Earth is recently presented (Saber [2013](#)) in which a dynamic geoid-like level is defined as an equipotential spherical surface as a counterpart

of the percolation parameter. When the hypothetical water level is decreased from the highest to lowest available heights on Earth, there occurs a geometrical phase transition at a certain critical level h_c around which the most parts of landmass join together – see Fig. 8. The most remarkable observation is that the critical level h_c coincides with the present mean sea level $h = 0$ on Earth.

The height relief $h(r, \theta, \phi)$ is assumed on a sphere of unit radius $r = 1$, which also coincides with the present mean sea level (as zero height level) on Earth. All corresponding lengths are expressed in units of the Earth's average radius.

Now imagine flooding this global landscape in a way that the continental land masses were crisscrossed by a series of narrow channels so that the resulting sea level all over the Earth would coincide with a spherical surface—the geoid. All parts above the water level are then colored differently as disjoint islands, and the rest is left white (Fig. 8). If the water level is high, there will be small disconnected islands, and if it is low, there will be disconnected lakes. However, there may be a critical value of the sea level $h = h_c$ at which a percolation transition takes place.

The usual order parameter is defined as the probability of any site to be part of the largest



Application of Percolation Theory to Statistical Topographies, Fig. 8 Schematic illustration of the continental aggregation by decreasing the sea level from top ($h = +100$ m) to bottom ($h = -80$ m). This shows a

remarkable percolation transition at the present mean sea level around which the major parts of the landmass join together

island. As shown in Fig. 9, the order parameter for islands has a sharp drop-off around the zero height level, i.e., right at the present mean sea level. According to the further evidence given in the following, it is an indicative of a geometrical phase transition at this level. The same analysis for the oceanic clusters (where disjoint oceans at each level are differently colored, leaving islands white) gives rise to a discontinuous jump in the oceanic order parameter at around -3640 m (Fig. 9).

Figure 10 illustrates two other percolation observables measured for Earth, the mean island size (analogous to the susceptibility of the system), and the correlation length. The mean island size χ is defined as

$$\chi = \frac{\sum'_s s^2 n_s(h)}{\sum'_s s n_s(h)}, \quad (3)$$

where $n_s(h)$ denotes the average number of islands of size s at level h , and the prime on the sums indicates the exclusion of the largest island in each measurement. The correlation length ξ is also defined as average distance of sites belonging to the same island,

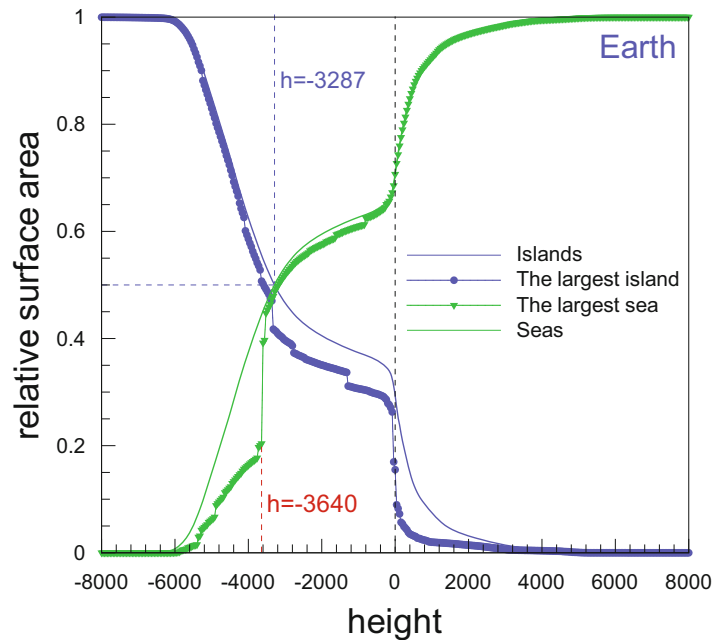
$$\xi^2 = \frac{\sum'_s 2R_s^2 s^2 n_s(h)}{\sum'_s s^2 n_s(h)}, \quad (4)$$

where R_s is the radius of gyration of a given s -cluster. As shown in Fig. 10, both quantities χ and ξ become divergent at the present mean sea level. The divergence of the correlation length is a signature of a phase transition at this level, implying that the critical fluctuations dominate at each length scale and that the system becomes scale invariant. The criticality of the current sea level justifies the appearance of the scale (and conformal) invariant features on Earth. These results provide a clear indication that water plays a more decisive role than has been imagined up to now to direct the tectonic movements and corresponding topographic evolutions.

According to the plate tectonic theory, the outer portion of Earth is made up of a number of distinct *plates* (Fig. 11) which move relative to each other. This motion is responsible for the major topographical features such as creation of oceans and pushing up mountain ranges. The open question motivated by this work is whether such an observed criticality plays the role of a geometric attractor for tectonic motions through geological time.

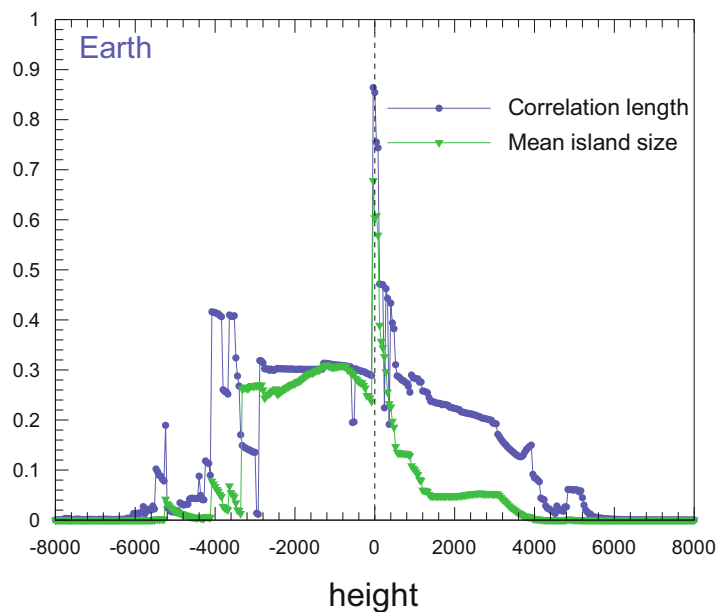
Application of Percolation Theory to Statistical Topographies,

Fig. 9 Relative surface area of the largest island (circles) and the largest sea (triangles) followed by the total surface area of the islands and the oceans (solid lines) to the total area 4π of the Earth, as a function of the sea level measured in meters. One critical level is distinguished by each order parameter. The oceanic critical level is close to the level $h = -3287$ m at which the total island and oceanic surface areas are equal



Application of Percolation Theory to Statistical Topographies,

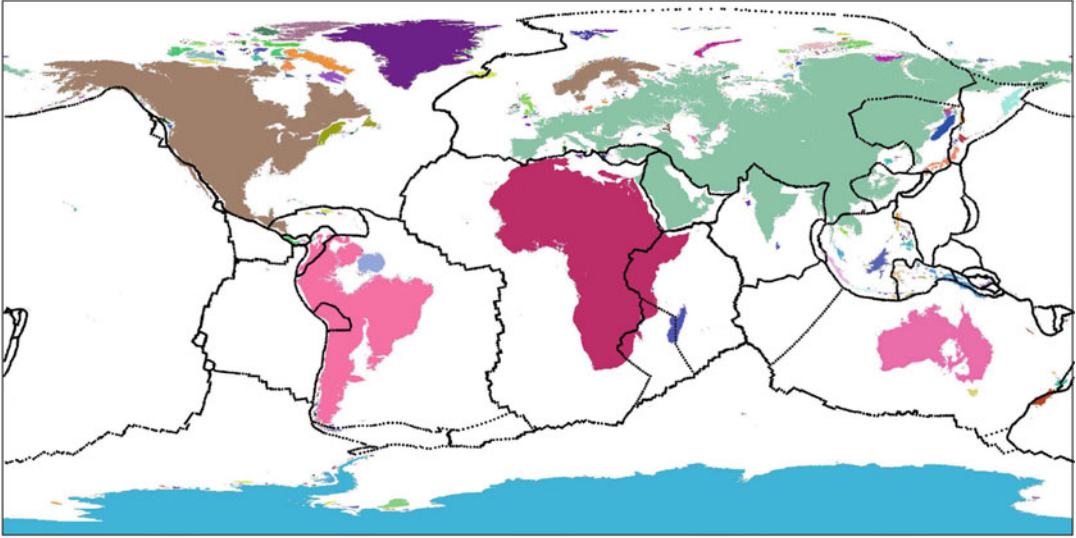
Fig. 10 Correlation length and mean island (land) size vs the sea level measured in meters, with a remarkable characterization of a geometrical phase transition at the present mean sea level (zero height level)



In the following section, we will discuss in more detail the order of the percolation transition observed on Earth's topography by combining network and percolation theory and then we identify and detect critical nodes at which an abrupt transition occurs during the evolution of the Earth's relief network.

Critical Nodes in Earth's Relief Network

In percolation on a lattice system, each lattice site (or bond) is occupied with probability p . A set of occupied sites in which every site is connected to its nearest neighbors forms a distinct cluster. In this section, starting from the topographic data



Application of Percolation Theory to Statistical Topographies, Fig. 11 Map of tectonic plates compared with different disjoint islands for the sea level at

$h = +100$ m. Every disjoint landmass is approximately surrounded by a major plate boundary

available in the ETOPO1 Global Relief Model, we first rank all the grid points according to their height $h(\phi_i, \theta_i)$ from the largest to the smallest value. A number is then assigned to each site according to the position of its height in the rank. The percolation model is defined as follows: Starting from an unoccupied lattice, the sites are occupied one by one according to their ranking, i.e., we first choose the site with the highest height, then the second, and so on. At each step, the fraction of occupied sites p increases by the inverse of the total number of sites N in the Earth's relief landscape. By this procedure, a configuration of occupied sites is continuously obtained at every p .

Next, we detect and quantify the clusters based on classical graph theory: A cluster is a subset of network nodes such that there exists at least one path from each node in the subset to another (Cohen and Havlin 2010; Newman 2010). To detect the clusters in evolving lattice system, one can use either the Hoshen–Kopelman algorithm (Hoshen and Kopelman 1976) or the efficient Newman–Ziff algorithm (Newman and Ziff 2000). We apply periodic boundary conditions along the zonal direction, and free boundary

conditions along the meridional direction. Each node has indeed four nearest neighbors. We denote G_m as a series of subnetworks. Due to the Earth's spherical shape, the largest cluster in the spatial relief network is defined as:

$$s_1 = \frac{\max \left[\sum_{i \in G_1} \cos(\phi_i), \dots, \sum_{i \in G_m} \cos(\phi_i), \dots \right]}{\sum_{i=1}^N \cos(\phi_i)}. \quad (5)$$

The system on a regular lattice is considered to be percolating if there is a path from one side of the lattice to the opposite side, passing only through the occupied links or nodes. When such a path exists, the component or cluster of sites that spans the network from side to side is called the spanning cluster. However, in many systems, such as on networks, no notion of “side” exists. For example, in our case here for Earth, in the zonal direction one cannot define the sides. However, when one looks at the behavior of the largest component containing $O(N)$ nodes or links, there will be a divergent correlation length and mean-island size at the largest gap in the order parameter (Fig. 10).

This evolving spatial relief network starts globally with N isolate nodes, and the nodes are occupied one by one according to their height h . We then analyze the dynamical evolution of the largest cluster s_1 in terms of the fraction of occupied nodes p . As shown in Fig. 12a, one finds that Earth's relief network undergoes several abrupt and statistically significant phase transitions, i.e., exhibiting a significant discontinuity in the order parameter s_1 . At each time step parameterized by p , one can define a gap, $g(p)$, corresponding to the successive evolution of the largest cluster, i.e.,

$$g(p) \equiv s_1(p) - s_1(p - 1/N). \quad (6)$$

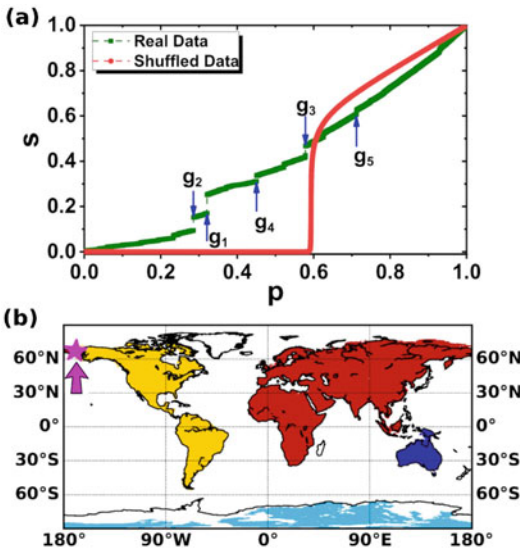
Therefore, g_1 indicates the largest gap, g_2 indicates the second largest gap, and so forth. The larger the gap g_i is, the larger are the two clusters before merging. Therefore, the largest gap g_i in

the order parameter is a natural candidate for a possible percolation transition and formation of a giant component of $O(N)$ nodes.

Figure 12b shows the network landmass clusters structure in the Earth's surface map at the percolation threshold (just before the largest gap that is indicated by the blue arrows with g_1). We find that the network, just before this jump, is characterized by four major communities – only clusters with size larger than 0.01 are shown – the largest one is the Afro-Eurasia continental landmass (shown by red), the second largest cluster is the Americas (shown by yellow), the third is located in Antarctica, and the fourth is Oceania. A critical node (64.458333°N , 171.141667°W) connects the largest and second largest cluster at the percolation threshold $p_c \approx 0.321$, with altitude level $h = -43$ m, under the current sea level.

Order of the Percolation Transition

To demonstrate that the observation of the jumps in the order parameter is not accidental, we analyze randomized topography obtained from the shuffling of the original data. This procedure removes the long-range correlations in the height profile while keeping the height distribution intact. A number of 100 such randomizations are considered to measure averaged giant cluster s , as shown in Fig. 12a. It has been also checked that the behavior for the shuffled data is independent of the realizations, and the same result is obtained for a single realization as well. As expected, the shuffled samples all correspond to the classical uncorrelated site percolation class with a continuous phase transition at $p \sim 0.59$. It has been pointed out that a random network or lattice system always undergoes a continuous percolation phase transition and shows standard scaling, features during a random process (Bollobás 2001). The question of whether percolation transitions could be discontinuous has attracted much attention recently in the context of interdependent networks (Buldyrev et al. 2010; Hu et al. 2011; Gao et al. 2012) and the so-called explosive percolation models (Achlioptas et al. 2009; Riordan and Warnke 2011; Fan et al. 2012; D'Souza and Nagler 2015). Interestingly, the dynamic evolution on our Earth's relief network indicates the



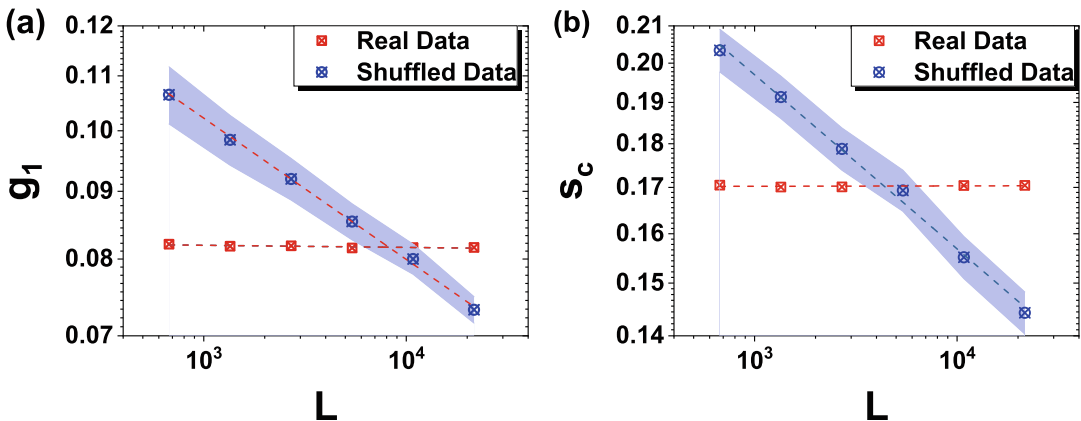
Application of Percolation Theory to Statistical Topographies, Fig. 12 (a) The largest landmass cluster relative size s_1 versus the fraction number of nodes/sites, p , for real (green) and shuffled (red) Earth's relief records. g_1 – g_5 indicate the largest five gaps, defined in Eq. 6. (b) Snapshots of the landmass clusters structure of the Earth surface topography network just before the percolation threshold (the largest jump at $p \approx 0.321$). Different colors represent different clusters; the grid resolution is 1 arc-minute; the star indicates the critical node. Only the clusters with relative size larger than 0.01 are shown

possibility of discontinuous phase transition, as shown in Fig. 12a. To further test the order of the percolation phase transition, one can study the finite-size effects of the network by altering the resolution of nodes. One then calculates $g_1(L)$, the largest gap in s as a function of network system size L , to see how it behaves when extrapolated to the infinite system size. L is defined as the number of nodes in the zonal direction. If $g_1(L)$ approaches zero as $L \rightarrow \infty$, the corresponding giant cluster is assumed to undergo a continuous percolation; otherwise, the corresponding percolation is assumed to be discontinuous (Nagler et al. 2011). The results are shown in Fig. 13a. It suggests a discontinuous percolation since $g_1(L)$ tends to be a nonzero constant. For comparison, the continuous results are shown for shuffled data with known critical exponents $\beta/\nu = 5/48 \approx 0.104$, where β is the critical exponent of the order parameter $s \sim |p - p_c|^\beta$, and ν describes the divergence of the correlation length $\xi \sim |p - p_c|^{-\nu}$. In addition, the scaling relation with size for the order parameter is examined at the percolation threshold (just before the largest jump g_1), $s_c \sim L^{d_f - d}$, for both real and shuffled data (see Fig. 13b). It has been found that $d_f - d = 0$, an indication of

discontinuous percolation for our real network; however, for the shuffled core from simulations, $d_f - d \approx -0.104$, which agrees well with the known exponent value for standard percolation in two dimensions, i.e., $d_f = 91/48$ (Stauffer and Aharony 1994; Sahimi 1994b). The dashed lines shown in Fig. 13 are the best-fit lines for the data with $R^2 > 0.98$.

Origin of the Discontinuity

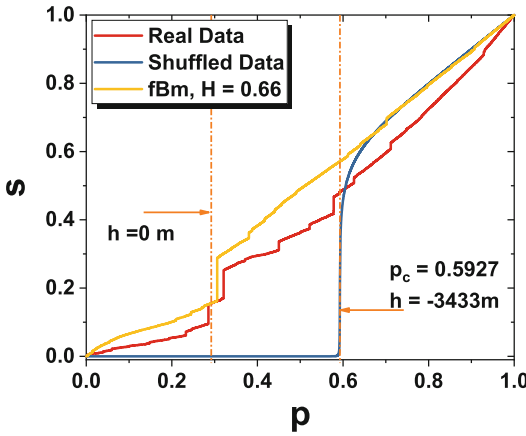
To better understand the Earth's topography and the origin of the discontinuity, let us examine the percolation on 2D fBm surfaces with Hurst exponent H . As explained in the previous sections, the Earth's rough surface can be modeled by fBm, with the estimation over the continental topography given by $H = 0.66$ (Gagnon et al. 2006). Application of the percolation analysis on fBm surfaces with $H = 0.66$ is shown in Fig. 14. Similar to the real network, one finds that s also exhibits abrupt transitions around p_c , whose position is sample-dependent. To further test the order of the percolation phase transitions on fBm surfaces, one can also use the finite-size scaling theory. The largest gap $g_1(H, L)$ (average) as a function of system size L is shown in Fig. 15a. One finds that percolation on fBm surfaces with



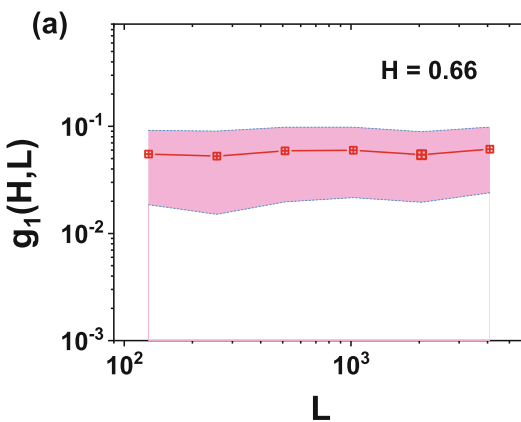
Application of Percolation Theory to Statistical Topographies, Fig. 13 Finite-size effects of the percolation in Earth's relief network. (a) Log-log plot of the largest gap g_1 vs the network system size L for original real data (red square) and shuffled data (blue circle). (b) Log-log plot of the largest landmass cluster relative size s_c at the percolation threshold vs L for real data (red square) and shuffled data (blue circle). For the real data, the slope

seems to approach zero, suggesting a discontinuous phase transition; for the shuffled data, the slope approaches -0.10 , which suggests a continuous phase transition with a known critical exponent $\beta/\nu = 5/48$ and $d - d_f = 5/48$. The dashed lines are the best-fit lines with $R^2 > 0.98$. The shaded regions correspond to error bars, which are calculated by the standard deviation

$H = 0.66$ is discontinuous, since $g_L(H, L)$ tends to be a nonzero constant for the very large extrapolated system size. One also finds that the location of the threshold is size-independent – Fig. 15b. This indicates that the percolation method can be used as an efficient tool to study the Earth's topography. The origin of the discontinuity might be explained by the long-range correlated behavior



Application of Percolation Theory to Statistical Topographies, Fig. 14 The largest landmass cluster relative size s vs the fraction number of nodes or sites, p , for real, shuffled, and 2D fractional Brownian motion (fBm) surfaces with $H = 0.66$. The two dashed lines indicate the sea level ($h = 0$ m) and the well-known site percolation threshold $p_c \approx 0.5927$, respectively

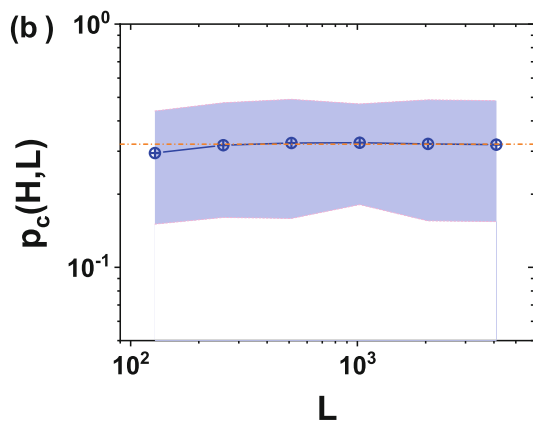


Application of Percolation Theory to Statistical Topographies, Fig. 15 The percolation on 2D fractional Brownian motion surfaces. (a) The average of the largest jump $g_L(H, L)$ as a function of system size L ; (b) the corresponding percolation threshold $p_c(H, L)$ as a function

of Earth's topography effectively induced by the long-wavelength activities such as the tectonic plates.

Future Directions

Mars shares many similarities and characteristics to Earth including various geological features and planetary structure. The remarkable bimodal distribution of elevations in both planets (Smith et al. 1999; Aharonson et al. 2001; Perotti and Rinaldi 2011) is one of the most striking global features suggesting similar geodynamic processes of crustal differentiation on Earth and Mars. There also exist several evidences (Parker et al. 1989, 1993; Baker et al. 1991; Clifford and Parker 2001; Head et al. 1998, 1999; Ivanov and Head 2001; Perron et al. 2007) for existence of an ancient Martian ocean in the northern hemisphere of Mars based on geographic features resembling ancient shorelines, which covers nearly one-third of the planet's surface. However, the interpretation of some features as ancient shorelines has been thoroughly challenged (Head et al. 1998, 1999; Carr and Head 2003) that left the existence of a primordial martian ocean controversial (Carr and Head 2003). Moreover, if oceans were formerly present on Mars, there is still a big



of L . The dashed line in (b) stands for the percolation threshold $p_c = 0.321$ for real data. Here, $H = 0.66$ is the Hurst exponent governing the correlations over the continental topography. The shaded regions correspond to error bars, estimated by the standard deviation

ambiguity about the volume of water with the estimations ranging over four orders of magnitude (Carr 1996; Luo et al. 2017). The analysis presented in this chapter on Earth's topography poses a natural question on possible application of the percolation theory to the martian topography in order to capture a connection between the global topographic features of Mars and its ancient geological evolution and structure.

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Elastic Percolation Networks

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Article Outline

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Bibliography

Glossary

Boson peak The Boson peak is an excess of low-frequency modes observed in glasses, as manifested, for example, in inelastic neutron scattering data. In rigidity percolation, the Boson peak is related to the number of floppy modes.

Constraint Edges in a graph constrain the degrees of freedom of the nodes in the graph. If edges are independent, each edge acts as one constraint.

Degrees of freedom In d dimensions, a point object has d degrees of freedom, while a body has $d(d + 1)/2$ degrees of freedom due to rotations and translations.

Floppy mode A floppy mode is a deformation of a structure which is soft and in ideal models is treated as a zero energy deformation.

Generic rigidity A network is generic if none of its edges are dependent due to the particular

geometric arrangement of the nodes in the network. With high probability random networks are generic, while regular lattices are nongeneric.

Isostatic network An isostatic network is rigid but has no redundant bonds. Isostatic networks are marginally rigid as removal of any edge induces a floppy mode. Ideal generic granular media are isostatic at jamming.

Redundant bond A redundant bond is not essential to the rigidity of a structure. Generic networks which contain redundant bonds are overconstrained and internally stressed.

Rigidity percolation threshold The rigidity threshold marks the transition from floppy networks which have zero elastic moduli to rigid networks with finite elastic moduli.

Definition of the Subject

Materials or structures with sufficiently low connectivity are floppy and have very low elastic moduli, while at high connectivity, they are rigid and have relatively high elastic moduli. Elastic percolation networks describe the transition from floppy to rigid that occurs as the network connectivity increases. The percolative geometry and elastic behavior near percolation are of particular interest. Conventional percolative geometries describe some experimental systems however the elastic critical behavior falls into several different universality classes. Moreover, distinct percolative geometries occur in systems with only central forces or which have soft torsional forces, and in these cases, both the geometry and elastic behavior may be distinct from conventional percolation. Granular media manifest a further distinct elastic percolation network, with the concept of an isostatic network underlying elastic behavior near jamming. This rich fundamental research framework is relevant to an enormous range of materials of scientific and technical interest (Thorpe and Duxbury 1999), including physical and chemical gels (Winter and

Mours 1997; Wyss et al. 2005), semiflexible networks in biology (Bausch and Kroy 2006; Kasza et al. 2007), proteins (Thorpe and Duxbury 1999), chalcogenide glasses (Boolchand et al. 2005; Thorpe and Duxbury 1999), and granular media (Wyart 2005). This brief review outlines the broad underlying principles common to these diverse systems.

Introduction

Many materials exhibit a sharp change in elastic behavior as the degree of interconnection in the material is increased. One well-studied example is the gel transition, in which a liquid becomes a gel (solid) as the number of short-range cross-links increases (de Gennes 1979; Flory 1953; Stauffer et al. 1982; Winter and Mours 1997; Wyss et al. 2005). A similar behavior occurs in epoxies where a polymer melt is irreversibly cross-linked by addition of cross-linking agents to form a stiff, hard solid (de Gennes 1979; Flory 1953; Serrano et al. 1990; Stauffer et al. 1982; Winter and Mours 1997). Cross-linking can be invoked using a variety of stimuli, including chemical, microwave, or thermal methods, given the appropriate precursors. Vulcanization in rubber formation is another example. Following the work by de Gennes (1976), there has been considerable debate about the elastic scaling behavior occurring near the gelation point. Semiflexible rod networks in biology, including actin filaments in the cell and F filaments in blood clots (Bausch and Kroy 2006; Kasza et al. 2007), are also gels. Moreover, paper is composed of cellulose rods and their cross-linking is critical to their mechanical performance (Alava and Niskanen 2006). As elucidated in sections “Idealized Experiments” to “Granular Media,” the ideas of floppy modes and network rigidity are useful in understanding the elastic behavior of these materials, particularly near the gel point.

Elastic percolation is richer than conductivity percolation in that transmission of stress is a vector process while transmission of current only requires simple connectivity. Nevertheless, in some cases, simple connectivity is sufficient to enable transmission of stress, while in others a more highly connected structure is required (Sahimi 1998;

Thorpe and Duxbury 1999). At the engineering level, the reasons for these distinctions have been known at least since the time of Maxwell (1864), though explicit models to elucidate the various types of elastic percolation processes in disordered media were only developed in the early 1980s (Feng and Sen 1984; Kantor and Webman 1984). Chalcogenide glasses, for example, $Se_{1-x}Ge_x$, are miscible and provide a unique system in which to study the effect of increasing the cross-linking of low coordination networks. Selenium is relatively floppy as it is twofold coordinated, while germanium is tetrahedrally bonded and rigid (Phillips 1979; Thorpe 1983). Though computational studies of these glasses indicate critical behavior near average coordination $r_c = 2.4$ (He and Thorpe 1985), the experimental consensus is for rather smooth elastic moduli near threshold, presumably due to rounding effects such as dihedral forces or entropic elasticity. Nevertheless, quantities such as the number of floppy modes in the Boson peak (Kamitakahara et al. 1991) and Raman scattering (Feng et al. 1997) do have a clear experimental signature near r_c .

The jamming transition of hard particles is different than the examples listed above as hard core repulsion provides a strong resistance to compression while there is no resistance to extension (Alexander 1998; Guyon et al. 1990; Moukarzel 1998; Wyart 2005). However in colloidal gels where there is a weak attractive potential, the behavior may be restored to that of rigidity percolation. Even in the absence of these attractive terms, some of the ideas of rigidity percolation are very useful in granular media, particularly the idea of an isostatic network (Donev et al. 2005; Moukarzel 1998). In this picture, the onset of rigidity in a granular packing occurs at a stress-free isostatic critical point. By considering systems with soft repulsive potentials, the elastic behavior in compression can be described by deviations from this critical point, as evident in recent large-scale computational studies (Ohern et al. 2003). Experiments generally support the idea of an isostatic critical point (Guyon et al. 1990; Majmudar et al. 2007; Wyart 2005).

The onset of elastic percolation can be determined by making realistic models and by studying their response to an applied stress. This strategy is

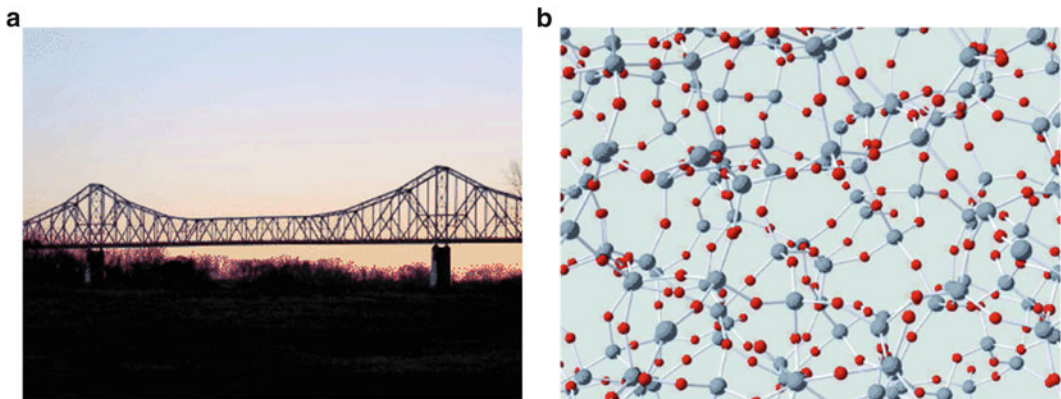
important; however, a deeper understanding has emerged through combinatorial methods which identify constraints that reduce the number of floppy modes (Jacobs and Thorpe 1995; Moukarzel and Duxbury 1995; Phillips 1979; Thorpe 1983). These constraint counting methods enable determination of the ability of a structure or graph to transmit stress, as developed by Maxwell for engineering structures (Maxwell 1864) (see Fig. 1). Understanding of stress-bearing geometries enables a broader view of elasticity percolation, unifying a broad range of experimental examples and elucidating the aspects which are universal and those that are not. It also enables unification of perspectives from several disciplines (as illustrated in Fig. 1), including engineering, mathematics, material science, physics, and more recently biological physics. Algorithms and concepts developed in the graph theory and topology communities have proved particularly rich (Hendrickson 1992; Laman 1970; Whiteley 2005). These methods and their relation to elastic percolation are surveyed in section “Exact Algorithms and Percolative Geometries.” Constraint counting methods also enable an exact analysis on Bethe lattices (Duxbury et al. 1999) which demonstrate that rigidity percolation is often first order (see section “Exact Solution on Bethe

Lattices”). From a theoretical perspective, replica symmetry breaking is not required in solving the rigidity percolation problem on Bethe lattices, though the system is frustrated (Duxbury et al. 1999; Rivoire and Barré 2006).

There are several different types of elastic percolation, depending on the interaction energy, as illustrated by considering standard force fields, such as the CHARMM (Brooks et al. 2004), AMBER (Wang et al. 2004), and the Dreiding (Mayo et al. 1990) potentials. They contain three short-range terms in their potential energy expressions, with a common form being

$$E = K_b \sum_{\text{bonds}} (b - b_0)^2 + K_\theta \sum_{\text{angles}} (\theta - \theta_0)^2 + K_\phi \sum_{\text{torsions}} (1 + \cos(n\phi - \phi_0)). \quad (1)$$

The first term in this expression describes the energy required to change the length of a nearest neighbor bond and is a central-force term, while the second and third terms provide a restoring force when bond angles or dihedral (torsion) angles are deformed. For the arguments that follow, we only need to be able to divide the energy into three terms so that



Elastic Percolation Networks, Fig. 1 Constraint counting methods are similar at the scale of bridges or atoms. (a) Maxwell asked how many beams are required to make engineering structures rigid. Triangulation is the standard method for ensuring enough central-force bonds (rods or beams) are available to support a load, as illustrated by the Cairo Mississippi River bridge from www.bridgehunter.com.

(b) Phillips (1979) asked how many higher coordination atoms are required to make a random network rigid, for example, a structure such as silica from www.phys.uu.nl/~Barkema. Dohler et al. (1980) showed that Maxwell counting implies that in bond-bending networks rigidity sets in when the average coordination is $r_c = 2.4$

$$E = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{torsions}}. \quad (2)$$

Even long-range nonbonded interaction terms can be represented using this type of model, by adding further neighbor bonds. The theoretical problem is as follows: Given a graph or network where the nodes interact with a potential such as Eq. 1, what is the elastic response? Where is the rigidity percolation threshold located as we increase the average connectivity of the network? How many floppy modes are there?

The most interesting geometric aspect of elastic percolation is that the geometry which can support a stress depends on the forces which are important, so that three different cases are illustrated by considering Eq. 1: (i) If all terms in Eq. 1 are important so that $K_b \sim K_\theta \sim K_\phi$, the underlying geometry is the same as connectivity percolation as any connected network transmits stress (see Fig. 2a); (ii) if only the first two terms are important (i.e., $K_b \sim K_\theta \gg K_\phi$), then the underlying geometry is a special sort of rigidity percolation which can be solved using efficient combinatorial methods (see Fig. 2b). This applies to many Chalcogenide glasses as well as to many polymers and proteins and is often called the bond-bending case. (iii) The hardest case is when only central-force terms are present (i.e., $K_b \gg K_\theta, K_\phi$) in three dimensions (see Fig. 2c). This problem is called the central-force rigidity problem and has no rigorous combinatorial characterization, so that we have to resort to direct simulations or approximations. Note that in two dimensions, the torsional term is absent and the central-force rigidity percolation problem can

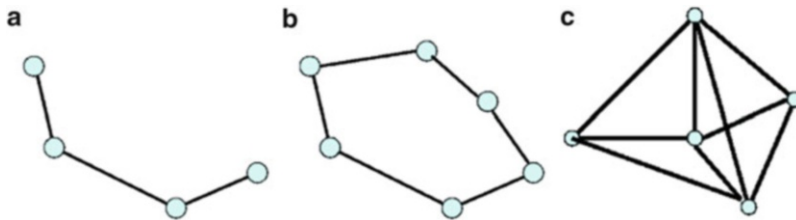
be solved using combinatorial methods (Hendrickson 1992; Jacobs and Hendrickson 1997; Moukarzel 1996).

It is intuitively evident that as the number of connections in a network increases, the system becomes more rigid or constrained. This intuitive observation is the basis of constraint counting methods introduced by James Clerk Maxwell in 1864 (Maxwell 1864), who asked the question: “how many edges are required to make a graph internally rigid, so that it can support an applied stress?” He made the following simple constraint counting argument for three-dimensional systems. Consider the case of central forces (only the first term in Eq. 1) and a set of “ n ” nodes connected by “ b ” bonds. Each node has three degrees of freedom, its three translations. If a graph is internally rigid, it still has six degrees of freedom due to its global translations and rotations. Maxwell then stated that the minimal number of bonds required to make a central-force system rigid is given by the relation

$$b = 3n - 6. \quad (3)$$

The example in Fig. 2c has $n = 5$ and $b = 9$ and so it satisfies this “Maxwell counting” condition. Maxwell counting is not exact, but it provides a useful mean field model for most rigidity problems. It can also be applied to connectivity percolation, but it is a much poorer approximation in that case.

In 1970, Laman (1970) proved a theorem showing that for a restricted class of rigidity problems, namely, planar graphs, a Maxwell counting



Elastic Percolation Networks, Fig. 2 Examples of networks which have just enough connectivity to be rigid. These structures are called isostatic and are stress free. They have a finite elastic constant and no floppy modes. (a) When central forces, bond angle forces, and dihedral

terms are all important (all three terms in Eq. 1 or 2). (b) When dihedral terms are not important (only the first two terms in Eq. 1 or 2 are important). (c) When only central forces are important (only the first term in Eq. 1 or 2)

calculation on subgraphs can be used to infer the rigidity of a graph. This revived interest in combinatorial rigidity and several methods for implementing his theorem were developed, with Hendrickson's (1992) bond-testing procedure yielding the highly efficient algorithms in use today. Extensions of Laman's theorem to body-bar networks and the conjecture of its extension to molecular frameworks (Jacobs 1998; Whiteley 2005) have yielded practical algorithms for a wide range of macromolecular systems and other networks. Maxwell's work is also important in engineering where truss networks are analogous to central-force systems and have a variety of applications (see, e.g., Fig. 1a).

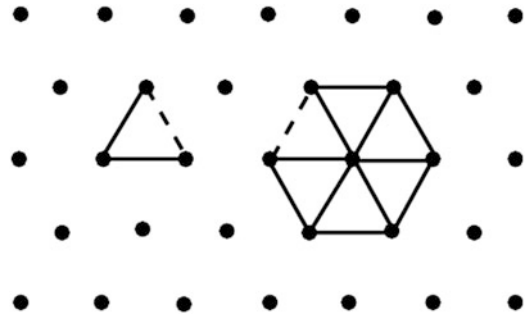
Basic Theoretical Concepts

Maxwell Counting in Random Networks

Maxwell counting (Phillips 1979; Thorpe 1983) provides a quick, and frequently quite accurate, estimate of the number of floppy modes and the rigidity threshold. For example, consider bond-diluted triangular lattices where a fraction p of bonds is present. Following Thorpe (1983), an unconstrained or flexible degree of freedom is called a floppy mode so that the number of floppy modes, F , remaining in a diluted triangular lattice is

$$F = 2N - \frac{1}{2}pzN + R, \quad (4)$$

where N is the number of nodes in the lattice, $z = 6$ is the coordination number of the lattice, and R is the number of redundant bonds. In this expression $2N$ is the number of degrees of freedom in the absence of any bonds, while $pzN/2$ is the number of bonds in the network. Maxwell counting sets $R = 0$ so that every bond added to the lattice reduces the number of floppy modes by one. Redundant bonds are not essential for the rigidity of a structure, though they do increase the elastic moduli and they may also induce internal stresses in rigidity percolation problems. A comparison of the simplest examples of redundant bonds occurring in connected and rigid clusters on a triangular lattice is presented in Fig. 3.



Elastic Percolation Networks, Fig. 3 The simplest subgraphs on a triangular lattice which contain a redundant bond (*dashed*). Connectivity case (*left*), $g = 2$ rigidity case (*right*) (From the article by C. Moukarzel and P. M. Duxbury in 1999)

In Maxwell counting we make the mean field approximation that the number of redundant bonds is zero and that the rigidity transition occurs when the number of floppy modes goes to zero. In that case, Eq. 4 predicts that the rigidity transition for bond-diluted triangular lattices occurs at $p_r = 2/3$. This is surprisingly accurate as large-scale simulations using methods which count the number of redundant bonds exactly determine the threshold $p_r = 0.6602(3)$ (Jacobs and Thorpe 1995) which is within 1 % of the Maxwell counting estimate. The percolation threshold for bond-bending systems is the same as that for connectivity percolation which is known exactly for bond-diluted triangular lattices, $p_c = 2 \sin(\pi/18) = 0.347 \dots$ It is then clear that the central-force rigidity threshold occurs at a much higher bond concentration than the connectivity threshold (Feng and Sen 1984). Note that the Maxwell estimate of the connectivity percolation threshold is found from $F = N - pzN/2$, yielding $p_c = 0.33$, which is a much poorer approximation than for the central-force rigidity case. In general Maxwell counting is a good approximation to the percolation threshold for all rigidity problems studied so far, except for cases where the connectivity percolation geometry applies!

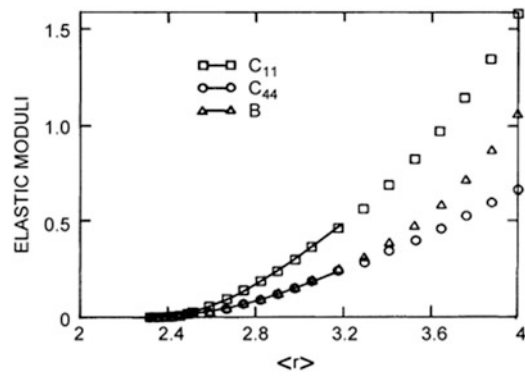
Though Maxwell counting is very useful, the fact that it ignores redundant bond makes it incomplete. A Bethe lattice approach (Duxbury et al. 1999; Moukarzel et al. 1997a) and field theory methods (Obukhov 1995; Rivoire and

Barré 2006) provide more complete theories. These approaches and also simulations on certain two- (Moukarzel and Duxbury 1990) and three-dimensional lattices (Chubynsky and Thorpe 2007), e.g., body-centered cubic lattices, have demonstrated that the rigidity percolation transition is frequently first order with a large jump in the infinite-cluster probability at the rigidity threshold. In fully random networks, the onset of an infinite rigid cluster and the onset of an internally stressed cluster occur at the same threshold. However, in several important cases, the infinite cluster is unstressed or isostatic which is believed to occur in granular media (Moukarzel 1998; Ohern et al. 2003) due to repulsive terms and in chalcogenide glasses due to self-organization (Boolchand et al. 2001; Thorpe et al. 2000). In these cases, a mixed transition may occur where a first-order jump and a continuous singularity occur at the same threshold. This behavior was first observed in Bethe lattice models of rigidity percolation (Moukarzel et al. 1997a).

Elastic Behavior

In all random connectivity and rigidity percolation problems studied so far, the elastic behavior is continuous near the rigidity threshold, even in cases where the infinite rigid cluster undergoes a first-order jump (Chubynsky and Thorpe 2007; Moukarzel and Duxbury 1990; Obukhov 1995). However, the question remains open in models of granular media and in self-organizing glass systems where an isostatic critical point plays a role. Direct numerical studies of the elastic constants of bond-diluted central-force systems indicate that they are quite linear for $p > p_c$ except very near the rigidity threshold, and that mean field estimates of the elastic behavior are surprisingly accurate in these cases (Feng and Sen 1984; Feng et al. 1985; Schwartz et al. 1985). In contrast the elastic behavior of bond-bending networks in three dimensions is nonlinear over most of the concentration range (see Fig. 4). Nevertheless, in all cases, the number of floppy modes as a function of $r < r_c$ is close to linear as is consistent with the simple Maxwell estimate.

In ideal elastic percolation networks, the elastic behavior is singular with a behavior typical of



Elastic Percolation Networks, Fig. 4 Elastic behavior of glass models as a function of average site coordination using continuous random network models like that of Fig. 1b (From He and Thorpe 1985)

a continuous singularity, $(p - p_c)^T$. The value of the critical exponent T has been a matter of debate. There is general agreement that in cases where bond-bending terms are dominant, the critical exponent T is larger than the conductivity exponent t (Kantor and Webman 1984). For example, in two-dimensional lattices with bond-bending terms, $t = 1.31(1)$ while $T = 3.96(3)$ (Zabolitzky et al. 1985). It is also well accepted that continuum systems may exhibit non-universal critical behavior due to the occurrence of necks of varying size in continuum systems (Feng et al. 1987). Moreover, even in the absence of continuum effects, there are several different elasticity models, with three well-studied cases being gel models where entropic effects are important (de Gennes 1976; Plischke et al. 1998) and following de Gennes, $T \approx t$; bonding-bending networks where $T \approx t + 2\nu$ (Bergman 2003; Feng and Sen 1984; Sahimi and Arbabi 1993b; Zabolitzky et al. 1985); and central-force networks where the elastic critical behavior is close to the bond-bending case (Hansen and Roux 1989; Sahimi and Arbabi 1993a), at least on regular lattices.

However, in connecting network geometry to elastic behavior in central-force networks and in three-dimensional networks without torsional forces, it is important to distinguish between generic networks and nongeneric networks. This distinction is noticed in granular media

where perfectly monodisperse spheres can form regular packings in two dimensions with average contact number six, while random packings, through jamming of regular or polydisperse spheres, have average contact number near four. The latter case is the generic case, while the former is the nongeneric case. Nongeneric systems are characterized by constraints which are degenerate and occur in the dynamical matrix as dependent equations. In network structures, they can occur as special sets of parallel bonds or series combinations of bonds pointing in the same direction (see section “[Exact Algorithms and Percolative Geometries](#)”). These configurations do not occur on random networks which are therefore generic. Regular lattices such as the triangular lattice are thus nongeneric, and the consequences of this on elasticity are still poorly understood.

Idealized Experiments

Idealized experiments have been carried out to test the prediction that for a given geometric structure, the elastic moduli have different critical exponents than those which apply to conductivity. A simple tabletop experiment to test this prediction was devised by Benguigui (1984). In his experiment, holes are drilled on a square grid in a metal sheet. The conductivity, σ , and Young’s modulus, C , were measured as a function of the remaining metal, ϕ . From these experiments the elastic exponent $T \approx 3.5$ and conductivity exponent $t \approx 1.3$ were extracted, which are in agreement with theoretical expectations in two dimensions, within the experimental uncertainty. Conductivity and elasticity measurements on sintered submicron silver powder aggregates (Deptuck et al. 1985) yielded $t = 2.15(25)$ and $T = 3.8(5)$, which agree with theoretical calculations on bond-bending networks in three dimensions which predict $T = t + 2\nu$ (Bergman 2003) and with simulations (Sahimi and Arbabi 1993b). To our knowledge there have been no idealized experiments on central-force systems or on systems without torsional forces in three dimensions.

Chalcogenide Glasses

Following Phillips and Thorpe (Dohler et al. 1980; Phillips 1979; Thorpe 1983), Maxwell counting for the number of floppy modes in the $Se_{1-x}Ge_x$ system proceeds as follows. Each atom has three degrees of freedom while each r -fold coordinated atom imposes $r/2$ central-force constraints and $2r - 3$ bond-bending constraints on the network. A twofold Se atom then imposes two constraints while a fourfold Ge atom imposes seven constraints. Here we assume that the torsional forces are negligible and the network is continuous with all atoms in one connected cluster. The Maxwell counting estimate for the number of floppy modes is then

$$F = 3N - 2(1 - x)N - 7xN \quad (5)$$

where N is the number of atoms in the network and $r = 2$ for Se while $r = 4$ for Ge so that the average coordination of a glass is $r = 4x + 2(1 - x)$. Equation 5 indicates that the number of floppy modes is linear in x and goes to zero at $x_c = 0.2$, which corresponds to the critical average coordination $r_c = 2.4$ (Dohler et al. 1980). This critical coordination also applies when a fraction y of threefold coordinated atoms are added to the model, as is relevant to the ternary $Se_{1-x-y}As_yGe_x$. In that case $F = 3N - 2(1 - x - y)N - 9yN/2 - 7xN$, and the average site coordination, $r = 2(1 - x - y) + 3y + 4x$. Of course torsional forces are nonzero in these materials and have to be considered in comparisons with experiment.

The prediction of critical coordination $r_c = 2.4$ in chalcogenide glasses stimulated a search for experimental signatures of rigidity percolation. Though early experiments indicated a singular behavior in the elastic constants near r_c , these results were later found to be due to experimental artifacts. Later experiments indicated that the elastic moduli of chalcogenides are smooth near r_c . However, the number of floppy modes (Kamitakahara et al. 1991) and an appropriately defined asymptotic glass transition temperature (Angell 2004) do clearly indicate a rigidity threshold. The number of floppy modes is manifested in

inelastic neutron scattering data (Kamitakahara et al. 1991) where a strong low-frequency peak, called the Boson peak, exists for $r < r_c$ (see Fig. 5). The number of modes in the Boson peak gives a measure of the number of floppy modes, and the location of the peak provides an estimate of the dihedral forces in the material. Theoretical analysis of the dynamical response of glassy networks yields good agreement with this data (Cai 1989). Several other measurements, including Mössbauer spectra (Bresser et al. 1986), Raman scattering (Feng et al. 1997), and vibrational lifetimes (Uebbing and Sievers 1996), also support a critical value of r_c which is close to 2.4.

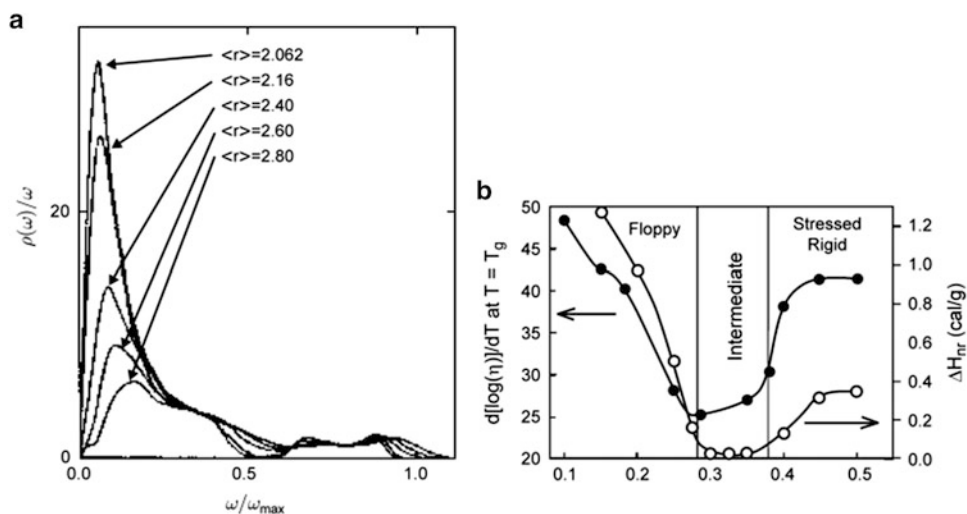
A stimulating, though still controversial, concept is the intermediate phase in chalcogenide glasses (Boolchand et al. 2001, 2005; Thorpe et al. 2000). The intermediate phase lies between the traditional floppy and rigid phases and occurs by self-organization to avoid internal stress. There are then two coordination thresholds r_1 and r_2 , with the first heralding the onset of a rigid but stress-free network and the second the onset of a rigid but internally stressed network (Thorpe et al. 2000). The extent of the intermediate regime between r_1 and r_2 has been explored in a variety

of models (Thorpe et al. 2000), and experimental support has come from studies of chalcogenide glasses over narrow composition regimes (Boolchand et al. 2001, 2005), as illustrated in Fig. 5b.

Constraint counting and rigidity concepts developed in chalcogenide glasses have been applied to a wide variety of covalently bonded materials, ranging from amorphous carbons to complex ternaries. Thermal effects along with local structural and chemical ordering often confound a simple interpretation of the data as a purely random rigidity percolation process; nevertheless, rigidity and elastic percolation concepts are fundamental to much of the literature in this area (Alexander 1998; Angell 2004; Thorpe and Duxbury 1999; Wyart 2005).

Gels and Semiflexible Rod Networks

Soon after the development of percolation theory, gelation was recognized as a related process, and the geometry of gels has been compared to percolation in many different systems (Bausch and Kroy 2006; Kasza et al. 2007; Martin et al.



Elastic Percolation Networks, Fig. 5 Evidence for rigidity percolation in chalcogenides. (a) The boson peak near the critical coordination $r_c \approx 2.4$. $\rho(\omega)$ is the density of inelastic neutron scattering modes at frequency ω (Kamitakahara et al. 1991). (b) Evidence for an

intermediate phase in the chalcogenide glasses $\text{Se}_{1-x}\text{As}_x$. The intermediate phase observed in the derivative of the viscosity $d\eta/dT$ at T_g and in the nonreversible enthalpy ΔH_{nr} . (From Boolchand et al. 2001)

1988; Rueb and Zukoski 1997; Stauffer et al. 1982; Winter and Mours 1997; Wyss et al. 2005; Xu et al. 2007). Though percolation provides a useful framework for the description of the onset of rigidity in gels, it is often difficult to access the critical regime (Ross-Murphy 2007).

Gels are ubiquitous in science, nature, and technology though there is no consensus definition of what constitutes a gel. Nevertheless, we are all familiar with gels, ranging from jelly to clay dispersions and to chemically cross-linked systems such as rubber and epoxies. Gelation may occur through physical or chemical cross-linking or through a combination of both processes. Cross-linking is a short-range concept and long-range forces can sometimes be critical. Nevertheless, a broad range of physical and chemical gels can be understood using rigidity concepts based on the change in structure as the cross-linking in a network increases. Even at the single-molecule level, it is sometimes reasonable to use rigidity percolation ideas to evaluate flexibility as a function of internal cross-linking, for example, in proteins (Rader et al. 2002). Colloidal gels with strong repulsive terms and weak short-range attractive interactions have many features in common with granular media, as described in the next section.

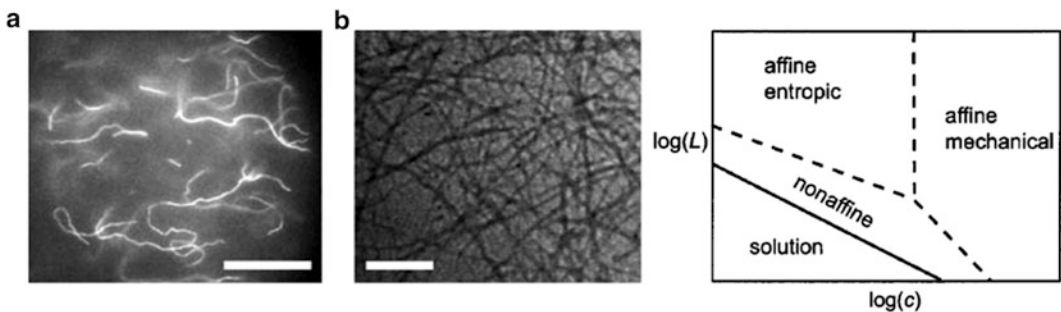
The original work on gels related the gelation point to connectivity percolation (Stauffer et al. 1982), while recent work relates the gel point in rod networks to rigidity percolation (Head et al.

2003; Heussinger and Frey 2006; LatvaKokko et al. 2001; LatvaKokko and Timonen 2001), as illustrated in Fig. 6. Maxwell counting in two-dimensional rod networks (LatvaKokko et al. 2001) states that the number of floppy modes in a network with N rods connected by P pivots is given by

$$F = 3N - 2P - 3. \quad (6)$$

There are three degrees of freedom per rod, two translations and one rotation, while each pivot removes two translational degrees of freedom from the two rods which it connects. The Maxwell counting estimate, found by setting $F = 0$ in Eq. 6, for the onset of rigidity in these two-dimensional rod networks is then $P_r/N = 3/2$, so that there are three pivot points on each rod. Connectivity percolation occurs at $P_c/N = 1$. Elastic models have been simulated and good agreement with Eq. 6 was found. However experimental gels exhibit correlations in local structure (Wyss et al. 2005) and in the case of fibers' orientational ordering and bundling (Bausch and Kroy 2006; Kasza et al. 2007). Moreover, the elastic behavior of cross-links is difficult to quantify. These factors are particularly important for non-universal parameters such as the percolation or gelation threshold, and they strongly affect the nonlinear response of gels.

The elastic behavior near gelation is expected to be more universal provided long-range



Elastic Percolation Networks, Fig. 6 Elastic percolation of biofibers. (a, b) Two views of the actin filament network in a human cell (From Tharmann et al. 2007). The right panel is a schematic phase diagram of semiflexible rod networks (From Head et al. 2003). The solid line is

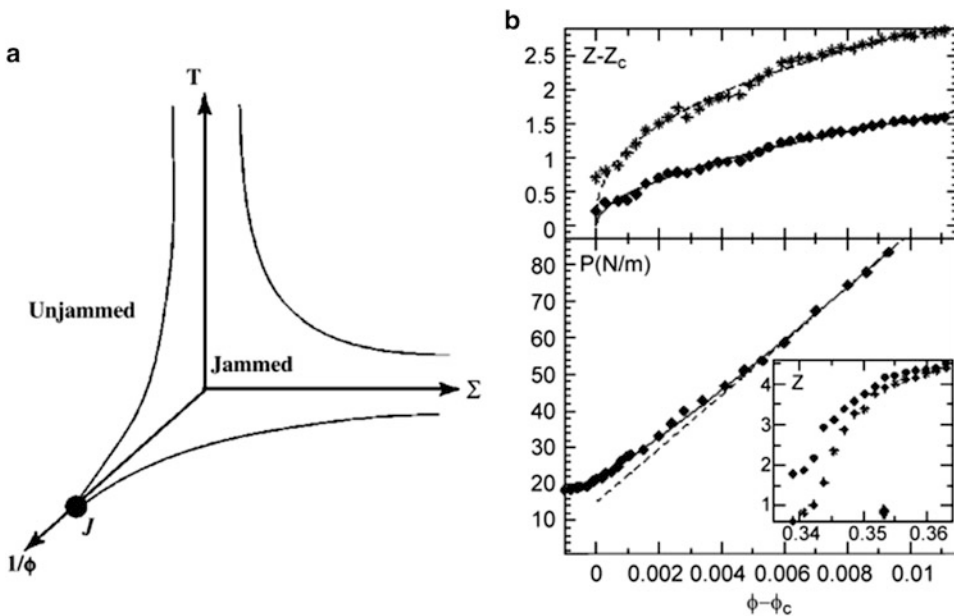
associated with a rigidity threshold in a random rod network. The mean distance between cross-links and entanglements is l_c , and $c \approx 1/l_c$. L is the molecular weight of the semiflexible polymers and the rigidity threshold occurs at $L \approx 1/c$ which defines the sol–gel transition in this model

correlations in structure are absent. In a well-known paper, de Gennes predicted that the elastic critical exponent, T , of gels should be the same as the conductivity exponent t (de Gennes 1976). However, as discussed in section “Basic Theoretical Concepts” and elaborated upon in section “Elastic Critical Behavior,” purely geometric models predict that the elasticity exponent is significantly larger than $t_{3D} = 2.01(1)$ and is well described by $T_{3D} = t_{3D} + 2\nu_{3D} = 3.77(3)$, where $\nu_{3D} = 0.88$ is the percolation correlation length exponent (Bergman 2003; Feng and Sen 1984; Kantor and Webman 1984; Sahimi and Arbabi 1993b; Zabolitzky et al. 1985). Over the years many experiments have measured T at the gelation threshold, for example, (Axelos and Kolb 1990; Grant and Russell 1993; Martin et al. 1988; Ross-Murphy 2007; Winter and Mours 1997; Wyss et al. 2005), with the consensus that $T = t$ in most gels as predicted by de Gennes. This issue will be discussed further in section “Elastic Critical Behavior.”

Granular Media

Jamming occurs as the packing fraction or density of a colloidal or granular system increases. Though the relations between rigidity and jamming have been discussed for many years (Guyon et al. 1990), it is only recently that the relationship has yielded to a clear quantitative analysis (Alexander 1998; Moukarzel 1998; Ohern et al. 2003; Wyart 2005). Alexander (1998) discussed the presence of floppy modes or rattlers in granular systems and recent work has noted their relation to the Boson peak in glasses (Wyart et al. 2005).

The presence of complex stress-bearing networks has been imaged (Guyon et al. 1990) and studied analytically and computationally, and the relation to an isostatic network was noted by Moukarzel (1998) who developed the idea of jamming as an isostatic critical point. Molecular dynamics simulations in systems with purely repulsive potentials provide a beautiful synthesis of the relations between rigidity, colloidal glasses, and granular media (Ohern et al. 2003) (see Fig. 7). These



Elastic Percolation Networks, Fig. 7 Behavior of (a) theoretical and (b) experimental dense packings near jamming. (a) Schematic of phase behavior found from simulations of purely repulsive models (From Ohern et al. 2003). The jamming point J is an isostatic critical point. Σ is the applied shear stress, T is temperature, and ϕ is

packing fraction. (b) Behavior of the pressure P and average coordination number $Z - Z_c$ on approach to jamming of photoelastic spheres. $\phi - \phi_c$ is the deviation from close packing (From Majmudar et al. 2007). In the top panel and in the inset, the diamonds exclude rattlers while the stars include them

simulations demonstrate that the zero-temperature jamming point provides insight into the whole phase diagram and enables calculation of the way in which various properties approach zero on approach to jamming from above. These simulations avoid the nongeneric critical point which is characteristic of the crystal phase of monodisperse packings and instead focused upon noncrystalline random packing states which are characteristic of generic rigidity. The computed critical exponents for the shear modulus depend on the form of the repulsive potential but not on the spatial dimension. Later simulations suggest that the stress-bearing backbone has a mixed behavior on approach to the jamming point, and its behavior is argued to be essentially the same as that observed in the Bethe lattice theory near an isostatic critical point (Schwarz et al. 2006). Experiments on photoelastic spheres (Majmudar et al. 2007) are in general supportive of the physical picture emerging from these theoretical insights (see Fig. 7), including the idea of a jump in average coordination at the jamming point.

Exact Solution on Bethe Lattices

Maxwell counting provides a very useful mean field theory for the rigidity transition; nevertheless, it is not a complete theory as it ignores redundant bonds and does not provide a geometry for the rigidity percolation process. Moreover, Maxwell counting predicts that the onset of rigidity occurs when all floppy modes are removed so that the whole network is in one giant isostatic cluster.

Bethe lattice theory is a more complete theory which resolves most of the problems with Maxwell counting methods; moreover it is simple and exactly solvable. In the following we describe the simplest Bethe lattice theory to illustrate the way in which the classic theory of connectivity percolation compares to rigidity percolation (Fisher and Essam 1961) and how Maxwell counting should be modified in light of the Bethe analysis. The extent of the intermediate phase (Thorpe et al. 2000) can also be simply calculated from the results of the Bethe lattice rigidity theory, as outlined at the end of this section.

The rigidity problem on Bethe lattices encompasses a wide range of different models (Moukarzel et al. 1997a), though here we focus on one generic case (Duxbury et al. 1999). In d dimensions a point object has d degrees of freedom (d translations), while extended objects or bodies also have rotational modes and a total of $d(d + 1)/2$ degrees of freedom. We define g as the number of degrees of freedom of a free or unbonded site, so that $g = 1$ corresponds to connectivity percolation, $g = d$ to point objects, and $g = d(d + 1)/2$ to bodies. A network with N sites (and no edges) has a total of $F = Ng$ degrees of freedom or floppy (zero frequency) modes. Constraint counting notes that each time an *independent* edge is added to the network, the number of floppy modes is reduced by one, so that

$$F = Ng - E + R \quad (7)$$

where E is the number of edges in the graph and R is the number of redundant edges. Note the additional term R on the right-hand side. This term is key in understanding the relation between constraint counting and percolation, and in finding algorithms for rigidity percolation. An edge does not reduce the number of floppy modes if it is placed between two sites which are already mutually rigid, in which case this edge is redundant. The simplest examples of subgraphs containing a redundant bond on a triangular lattice are illustrated in Fig. 3 for the connectivity ($g = 1$) and $g = 2$ rigidity cases. Note that any one of the bonds in these structures could be labeled as the redundant one. However, once any one of them is removed, all of the others are necessary to ensure the mutual rigidity of the structure. The set of all bonds which are mutually redundant form an overconstrained or stressed cluster. In rigidity theory each edge can be considered to be a central-force spring, which means that there is a restoring force only in tension and compression. Then an overconstrained cluster of such springs (with random natural lengths) is internally stressed due to a redundant bond. In the connectivity case, each bond is like a wire which can carry current or fluid flow. The simplest overconstrained cluster is then a loop which can support an internal eddy

current. Rigid structures which contain no redundant bonds are minimally rigid or isostatic. In connectivity percolation, isostatic structures are trees, whereas in ($g > 1$) rigidity percolation, isostatic structures always contain many loops.

In percolation problems, we are interested in the asymptotic limit of very large graphs ($N \rightarrow \infty$), and it is more convenient to work with intensive quantities, so we define $f(p) = F/gN$ and $r(p) = 2R/gzN$, so that

$$f(p) = 1 - \frac{z}{2g}(p - r(p)) \quad (8)$$

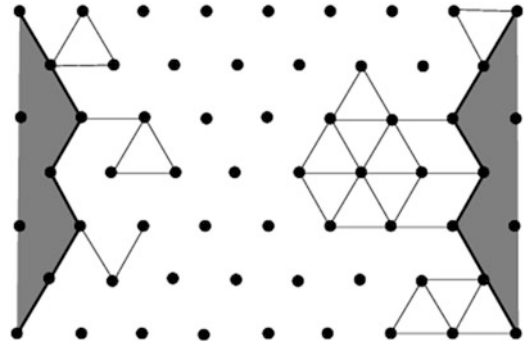
where, on average, the number of edges is $E/N = zp/2$. $g * r(p)$ is the probability that a bond is redundant (Duxbury et al. 1999; Jacobs and Thorpe 1995). The number of floppy modes, $f(p)$, acts as a free energy for both connectivity and rigidity problems, so that if $\partial f(p)/\partial p$ undergoes a jump discontinuity, the transition is first order (Duxbury et al. 1999). The behavior of this quantity is directly related to the probability that a bond is overconstrained P_{ov} via the relation

$$\frac{\partial f}{\partial p} = -\frac{z}{2g}(1 - P_{ov}). \quad (9)$$

If the transition is second order, the second derivative $\partial^2 f/\partial p^2 \sim (p - p_c)^{-\alpha}$, where α is the specific heat exponent (Jacobs and Thorpe 1995).

The infinite-cluster probability in rigidity problems is composed of the stress-bearing backbone plus dangling ends. Dangling ends are rigidly connected to the backbone but are not part of the stress-bearing backbone. Examples of dangling ends in the connectivity and rigidity cases are illustrated in Fig. 8 for central-force problems on the triangular lattice.

The quantities, $f(p)$, $\partial f(p)/\partial p$, $r(p)$, P_{∞} , P_{ov} can be calculated exactly on Bethe lattices of general coordination z , where p is the bond probability of the Bethe lattice. The key quantity from which all the others is derived is the probability, T , that a site on a branch of a Bethe lattice is part of the infinite rigid cluster. This quantity has a steady-state solution which is found from the equation



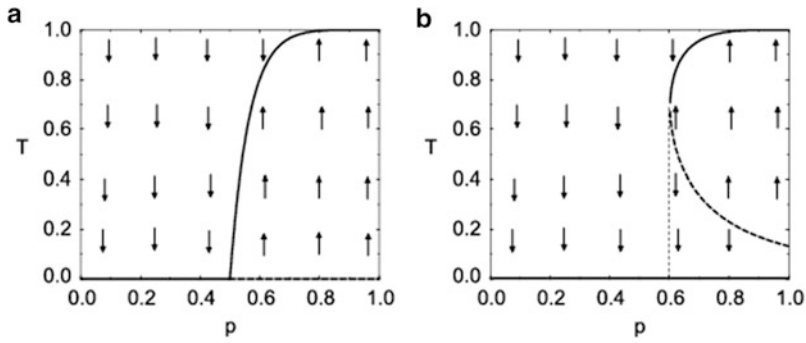
Elastic Percolation Networks, Fig. 8 Dangling ends connected to a backbone (shaded). Connectivity case (left) and $g = 2$ rigidity case (right). Dangling ends do not contribute to current (left) or stress (right) which is applied in the vertical direction

$$T = \sum_{l=g}^{z-1} \binom{z-1}{l} (pT)^l (1-pT)^{z-1-l}, \quad (10)$$

where T is the probability that a site is connected to the infinite rigid cluster through one branch of the Bethe lattice. The case $g = 1$ recovers the well-known Bethe lattice equation for connectivity percolation (Fisher and Essam 1961), while for general g , these equations are the same as those for k -core percolation on Bethe lattices (Chalupa et al. 1979), where $k = g + 1$. As illustrated in Fig. 9, the solutions to Eq. 10 depend sensitively on the value of g . The case $g = 1$ corresponds to connectivity percolation and shows a typical continuous behavior, while the case $g = 2$ is first order and is typical of all cases where $g > 1$. This means that central-force percolation on random graphs is typically first order (Duxbury et al. 1999; Moukarzel et al. 1997b).

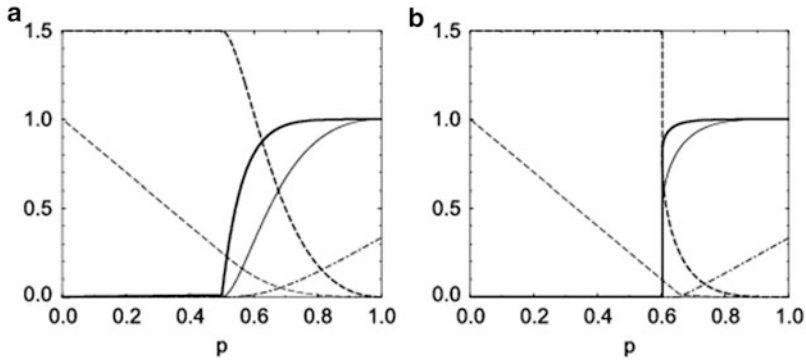
It is clearly seen from these figures that the rigidity transition is first order on Bethe lattices, while the connectivity transition is second order. We identify the point at which the stable solution becomes nonzero as p_s , the spinodal point, and in the connectivity case $p_s = p_c$ because the transition is second order.

Combining the stable solutions to branch probabilities yields the infinite-cluster probability of the Bethe lattice



Elastic Percolation Networks, Fig. 9 Domains of attraction of the mean field equations, Eq. 10. (a) A typical connectivity percolation behavior (this example is $z = 3$) and (b) a typical rigidity percolation behavior

(this example is $z = 6$, $g = 2$). Dark lines are stable (attractive) solutions and the dashed line is unstable (From the article by C. Moukarzel and P. Duxbury in Thorpe and Duxbury (1999))



Elastic Percolation Networks, Fig. 10 The order parameters, floppy modes, and its derivative as a function of p for (a) a typical connectivity percolation case $z = 3$, $g = 1$ and (b) a typical rigidity percolation case, $z = 6$, $g = 2$. The quantities plotted are $f(p)$ (dashed), $r(p)$ (dot dashed), $-df/dp$ (heavy dashed), P_{ov} (thin solid), P_{inf}

(heavy solid). In the connectivity case, we find $p_c = p_s$, while in rigidity cases $p_s < p_c$. For the rigidity case, $p_s = 0.605$ and $p_c = 0.655$ (From the article by C. Moukarzel and P. M. Duxbury in Thorpe and Duxbury (1999))

$$P_{\infty} = \sum_{l=g}^z \binom{z}{l} (pT)^l (1-pT)^{z-1}. \quad (11)$$

$$\frac{\partial f}{\partial p} = -\frac{z}{2g} (1 - T^2). \quad (13)$$

The other quantities of interest are found from the stable solution for T as follows. The probability that a bond is overconstrained is (Duxbury et al. 1999)

$$P_{ov} = T^2, \quad (12)$$

so that Eq. 9 yields

The probability that a bond is on the infinite cluster is

$$P_{inf} = T^2 + 2TT_1. \quad (14)$$

where T_1 is the probability that a site has one degree of freedom and can also be found straightforwardly (Duxbury et al. 1999). We also want to find the total number of redundant bonds $r(p)$ and

the total number of floppy modes $f(p)$. In order to find these quantities, we integrate Eq. 13 and then use Eq. 7. However, the integration of Eq. 13 leads to one free constant. To determine this constant, for a lattice of coordination z , we impose the constraint (Duxbury et al. 1999)

$$r(1) = 1 - \frac{2g}{z}. \quad (15)$$

We then find that $r(p)$ approaches zero at a critical point p_c , which lies above p_s , for any $g > 1$, and that p_c is close to the Maxwell estimate $p_c = 2g/z$. Results for five key quantities found from Bethe lattice theory are presented in Fig. 10 for typical conductivity and rigidity percolation cases.

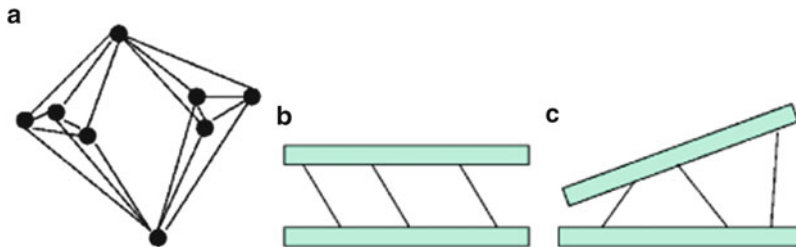
The Bethe lattice theory outlined above has been carefully compared with exact simulations of random graphs which demonstrate that it is exact (Duxbury et al. 1999). This is a symmetric theory as the order parameter does not need to be described by a nontrivial distribution. The fact that this symmetric theory is exact (Rivoire and Barré 2006) and yet applies to glassy systems such as granular media and rod networks is intriguing as replica symmetry breaking would be expected in those cases, as occurs in problems such as KSAT, spin glasses, and lattice gases. It is worth noting that the Bethe lattice Eqs. 10 and 11 are the same as the Bethe lattice equations for k -core percolation (Chalupa et al. 1979) which is also being used as a simple model for granular media (Schwarz et al. 2006). Extensions of the

Bethe lattice theory to chalcogenide glasses have been carried out and provide a more complete theory than Maxwell counting (Thorpe and Duxbury 1999).

Extension to the Intermediate Phase

In the intermediate phase (Thorpe et al. 2000), the network is dominated by a giant rigid but isostatic cluster. To generate such a cluster, we consider adding bonds to a graph, with the constraint that any redundant bond is not added to the network. As described in the next section, this is how the exact constraint counting algorithms proceed, so computation of geometric structures which are stress free is straightforward using Hendrickson's bond-testing procedure (Hendrickson 1992).

In the Bethe lattice solution, the onset of a metastable solution occurs at p_s ; however, this solution contains a number, $r(p_s)$, of redundant bonds. Since bonds are added randomly, the lowest threshold at which a stress-free percolating cluster can occur is $p_1 = p_s - r(p_s)$. In first-order rigidity cases, $r(p_s)$ is small, so to a good approximation $p_1 \approx p_s$. The upper limit of the intermediate phase is an isostatic network to which no more isostatic bonds can be added. This is just the Maxwell counting estimate, so $p_2 \approx p_m$. Calculation of p_1 and p_2 for other graphs and lattices can be carried out in a similar way, using the exact algorithms outlined in the next subsection. In second-order cases, however, $p_s = p_c$, so that $p_1 = p_c - r(p_c)$ and $p_2 = p_m$. In glasses, it is unlikely that all stress-inducing bonds



Elastic Percolation Networks, Fig. 11 Illustration of two key issues in combinatorial rigidity. (a) The double-banana configuration which violates Laman's theorem and illustrates a difficulty in applying combinatorial rigidity to three-dimensional central-force networks. (b) Nongeneric and (c) generic geometric structures. Laman's theorem and

its extensions apply only to generic networks. The non-generic case depends on geometry and so a theory depending only on connectivity is insufficient. The probability of finding nongeneric configurations in large random structures is negligible so generic rigidity applies

can be avoided so we expect the observed values of the intermediate regime to begin at $p > p_1$ and to end at $p < p_2$.

Exact Algorithms and Percolative Geometries

Exact constraint counting provides a procedure for figuring out if a structure can carry stress, without having to solve the elastic equations for the structure. The procedure is based on determining whether all internal degrees of freedom in the structure are fixed by the constraints. A small activity in this area has been ongoing for many years in the graph theory and topology branches of mathematics. The problem is called the graph rigidity problem and is a subset of the problem of graphic matroids. Laman's theorem in 1970 (Laman 1970) provides the basis for practical algorithms and states: A bar-joint graph in the plane is rigid *iff* it has no redundant bonds and $b = 2n - 3$, where b is the number of edges (bars) in the graph and n is the number of nodes. This is basically Maxwell counting (see Eq. 3) in two dimensions, modified by the key requirement that there be no redundant bonds. Hendrickson (1992) provided a practical algorithm which tests if a bond in a graph is redundant. In his algorithm, edges are added to the graph one at a time and tested to see if they are redundant. If they are redundant, then they are not placed in the structure but are noted and stored elsewhere. In this way an isostatic graph obeying Maxwell counting is generated. A structure with no redundant bonds has the Maxwell counting value, $F = 2n - b - 3$, of floppy modes. The number of redundant bonds is also counted enabling a check of the relation Eq. 7. It is also possible to use this method to find the number of stressed bonds, as when a redundant bond is added to a network, an internally stressed cluster of bonds is generated. By cleverly adding a redundant bond across the whole network, this can also be used to identify the stressed backbone (Jacobs and Hendrickson 1997; Moukarzel 1996).

Laman's theorem has been extended to body-bar systems in arbitrary dimensions (Tay 1984;

Tay and Whiteley 1985). There is also a conjecture that it is exact for molecular frameworks which is important in applications to chalcogenide glasses, polymers, and proteins (Jacobs 1998; Whiteley 2005). Molecular frameworks are systems where central forces and bond-bending terms are strong but torsional terms are neglected. However, a key system where no combinatorial characterization is available is the central-force rigidity problem in three dimensions where exceptions to Laman's theorem are known to exist, such as the famous double-banana configuration of Fig. 11a.

A second issue, of significance to a variety of applications including granular media, is the issue of generic rigidity as compared to nongeneric rigidity. The issue is illustrated in Fig. 11 where two examples of systems with two bodies and three bars in two dimensions are compared. In the generic rigidity case of Fig. 11c, the three bars have different lengths and are at different angles. Maxwell counting indicates that this system is rigid as there are three degrees of freedom per body and there are three bars. However, the nongeneric example in Fig. 11b is not rigid as the three bars are parallel enabling a shear distortion of the two bodies with respect to each other. The three bars, which are the constraints in this system, are not independent, and this dependence is due to the particular way in which the bars are arranged. In this nongeneric case, it is not sufficient to know only the connectivity of the graph as the particular geometry of the structure plays a key role. Clearly regular lattices and regular packings of granular media are nongeneric, while random lattices, polydisperse packings, and random packings are typically generic. Combinatorial rigidity applies to generic cases so that disorder in some sense makes the generic problem more tractable.

To illustrate Hendrickson's redundant bond-testing procedure, we consider percolation on diluted triangular lattices. The procedure applies to both rigidity and connectivity cases, and it is useful to compare the way in which bond testing compares in the two cases. In the connectivity case, Hendrickson's algorithm checks for loops. His redundant bond-testing procedure is based on bipartite matching which is a well-known

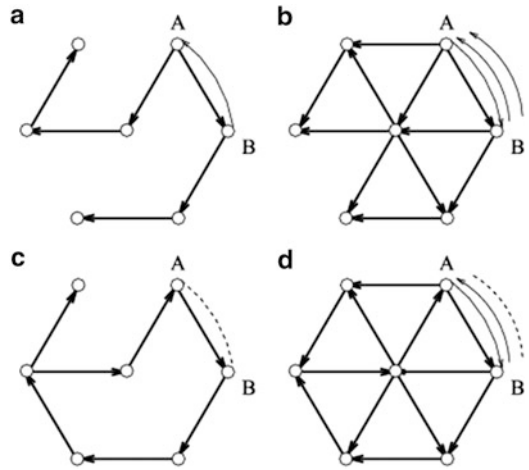
problem in combinatorial optimization. It is implemented as follows (Hendrickson 1992; Jacobs and Hendrickson 1997; Moukarzel 1996):

Start with an empty triangular lattice (no bonds) and assign to each node g degrees of freedom. *Then:*

1. Randomly add a bond to the lattice.
2. Test whether this bond is redundant with respect to the bonds which are currently in the lattice.
3. If the bond is redundant, *do not add it to the lattice*, but instead store its location in a different array.
4. Return to 1.

End

Step 2 is the key one and is implemented by matching constraints (bonds) to degrees of freedom, with the restriction that the number of constraints assigned to each node must be less than or equal to the number of degrees of freedom at a node ($g = 2$). It is natural to represent the assignment of constraints to nodes using arrows as illustrated in Fig. 12. When a new bond is added, we add $G + 1$ bonds to take account of the global translations and rotations of a body. For a triangular lattice, a body has three degrees of freedom, so we add four bonds as indicated in the figure. Hendrickson noted that if the $G + 1$ added bonds can be matched to the degrees of freedom in the graph, then the bond is not redundant. However, if the arrows cannot be matched, the added edge is *redundant*. Another useful way to think about the matching procedure is to consider associating pebbles with the degrees of freedom of the nodes in a graph. Then these pebbles may be placed on the edges of the graph with the constraint that they may only cover edges which enter the node. The matching of arrows to nodes then corresponds to placing pebbles on edges, with the constraint that pebbles can only sit on adjacent edges. The matching fails if it is not possible to cover all edges with pebbles (Jacobs and Thorpe 1995). A successful and a failed match are illustrated in Fig. 12 for a connectivity ($g = 1$) case and a rigidity ($g = 2$) case. Note that the bond that is being tested carries with it G additional copies



Elastic Percolation Networks, Fig. 12 Examples of successful (*top* figures, **a** and **b**) and failed (*bottom* figures, **c** and **d**) matches in the connectivity ($g = G = 1$, *left* figures, **a** and **c**) and joint-bar rigidity ($g = 2$, $G = 3$, *right* figures, **b** and **d**) cases on triangular lattices. AB is the new bond that is being tested. Each site has g degrees of freedom and therefore accepts at most g incoming arrows. Each new bond carries with it G auxiliary arrows, which must also be matched. If any of the arrows cannot be matched (*dashed*), the new bond is redundant (From the article by C. Moukarzel and P. M. Duxbury in Thorpe and Duxbury (1999))

which account for global degrees of freedom of a rigid cluster. In the connectivity case, $G = 1$, while on central-force bar-joint networks in two dimensions, $G = 3$.

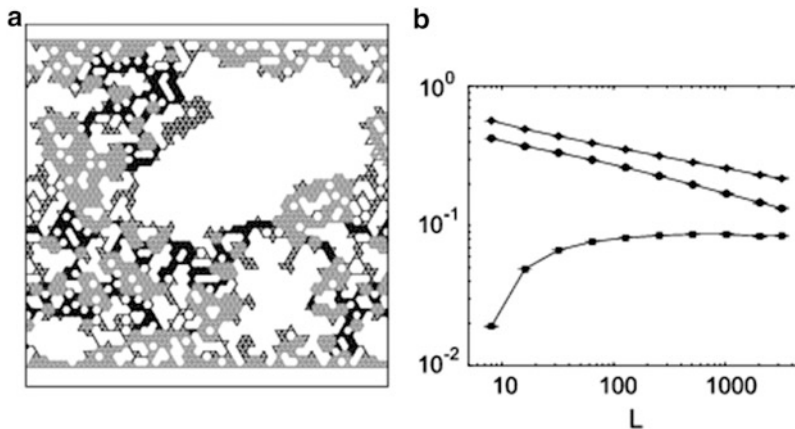
When the bond test fails, the algorithm identifies all bonds which are overconstrained or stressed with respect to the redundant bond. This set of bonds is called a *Laman subgraph*. Note that if a redundant bond is already in a graph, it is not possible to add a new bond and test its redundancy with this method. This is the reason that the algorithm proceeds by adding bonds one at a time starting with an empty lattice. Any error in testing the redundancy of a bond invalidates the rest of the addition sequence. However, since this algorithm is an integer method, there is no problem with roundoff. It is easy to see that the matching algorithm is quite efficient; however, it requires quite a bit of effort to fully optimize these methods. A key step in this optimization procedure is to identify rigid clusters and to describe them in a more condensed way. Moukarzel (1996)

condenses rigid clusters to a body and hence renormalizes an original bar-joint network to an effective body-joint-bar network. Jacobs and Hendrickson (1997) instead uses a reduced bar-joint representation of rigid subgraphs. In either case the computational complexity is reduced significantly especially for $p > p_r$.

The geometry of rigidity percolation on a triangular lattice is presented in Fig. 13 (Moukarzel and Duxbury 1990). Because of the fact that we add bonds one at a time until the percolation point is reached, it is possible to identify p_c or p_r exactly for each sample and therefore measure the components of the spanning cluster exactly at p_c or p_r . This eliminates the error associated with measurements at fixed values of p , since estimated exponents are known to depend very sensitively on p . Just as in connectivity percolation, at p_r we identify three different types of bonds: *backbone bonds*, *dangling ends*, and *cutting bonds*, as illustrated in Fig. 13a. These together form the *infinite cluster*. The cutting bonds are stressed (belong to the backbone), but they are “critical” because if one of them is removed, load is no longer transmitted across the infinite cluster.

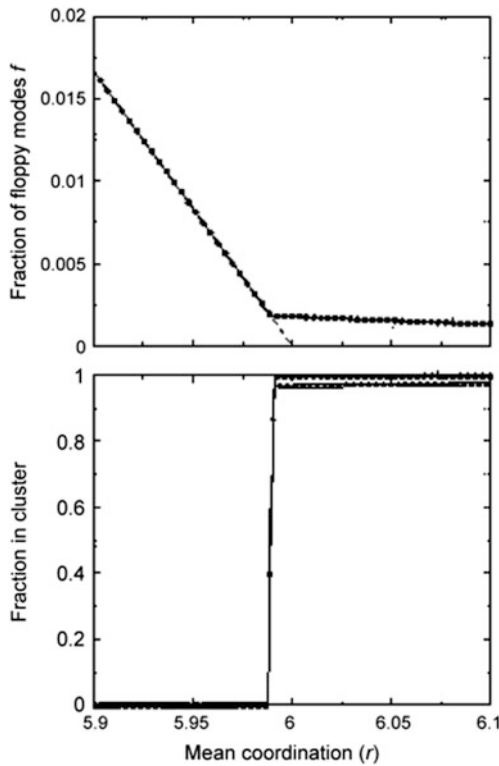
In order to find the correlation length exponent, two relations were used (Jacobs and Thorpe 1995, 1996; Moukarzel and Duxbury 1990, 1995): The size dependence of the threshold behaves as $\delta p_c \sim L^{-1/\nu}$, and secondly, the number of cutting bonds varies as $n_c \sim L^{1/\nu}$, yielding $\nu = 1.16(2)$ (Moukarzel and Duxbury 1995) or $\nu = 1.20(3)$ (Jacobs and Thorpe 1995). Calculations on the rigidity of rod networks (LatvaKokko et al. 2001) find $\nu = 1.18(2)$. From data such as Fig. 13b, the backbone density is found to decrease algebraically $P_B \sim L^{-\beta'/\nu}$, with $\beta' = 0.25 \pm 0.02$ (Moukarzel and Duxbury 1990, 1995; Moukarzel et al. 1997b). It also appears that the infinite-cluster probability is decreasing algebraically; however, that is difficult to reconcile with the behavior of the dangling ends which must also eventually decrease for this trend to be asymptotic.

Since it has a diverging correlation length, rigidity percolation on triangular lattices is second order; however, first-order cases do occur in two dimensions, for example, a square network to which diagonals are added at random locations exhibits a strong first-order transition, even



Elastic Percolation Networks, Fig. 13 The geometry of rigidity percolation on site-diluted triangular lattices. (a) The infinite-cluster geometry at threshold. *Dark wide lines* are cutting bonds, *wide lines* are noncritical backbone bonds (blobs), and *thin lines* are dangling ends. (b) The density of backbone bonds (*circles*), infinite-cluster bonds (*diamonds*), and dangling bonds (*squares*) at p_r . A fit to the backbone density yields the exponent $P_B \approx L^{-\beta'/\nu}$, with

$\beta' = 0.25(2)$. The dangling ends have not reached the asymptotic regime so it is not clear if the infinite-cluster probability has either. Nevertheless, the transition is second order with correlation length exponent $\nu = 1.16(2)$ found from the finite-size scaling of the number of cutting bonds and also from the scaling of finite-size corrections to p_c (Jacobs and Thorpe 1996; Moukarzel and Duxbury 1990, 1995) (From Moukarzel and Duxbury 1990)



Elastic Percolation Networks, Fig. 14 The number of floppy modes (*top panel*). The infinite-cluster probability and stressed backbone probability (*bottom panel*) on bond-diluted bcc lattices. The transition is strongly first order, though the elastic behavior appears to be continuous (From Chubynsky and Thorpe 2007)

though the elastic behavior remains continuous (Moukarzel and Duxbury 1990; Obukhov 1995). Moreover, simulations of central-force networks in three dimensions (Chubynsky and Thorpe 2007) demonstrate a strong first-order transition, as illustrated in Fig. 14.

Elastic Critical Behavior

After a flurry of activity in the 1980s and early 1990s, the study of elastic critical exponents has diminished; nevertheless, many issues remain unresolved. The distinction between bond-bending networks and central-force networks was brought into sharp focus in the early 1980s (Feng and Sen 1984); moreover, the distinction between the critical exponents describing

conductivity and elasticity was emphasized (Kantor and Webman 1984). Many studies were purely energetic, so that thermal effects were ignored. In contrast, de Gennes' (1976) early argument concerning the equivalence of the conductivity and elasticity exponents of gels relies on entropic springs. The effect of entropic terms has been simulated more recently, supporting the early analysis by de Gennes (Plischke 2006; Plischke and Joos 1998).

In two-dimensional systems with bond-bending terms or in three-dimensional systems with both bond-bending and torsion or dihedral terms (see Eq. 1), elastic percolation occurs at the conductivity percolation threshold. In the absence of entropic terms, it is well established that in this case the elastic critical behavior, $E \sim (\delta p)^T$, is different than the conductivity critical behavior, $\sigma \sim (\delta p)^t$. E is the Young's modulus while σ is the conductivity, and $\delta p = p - p_c$ with p_c the conductivity percolation threshold. T is the elastic critical exponent and t is the conductivity critical exponent. A variety of methods have been applied to the calculation of t and T in two and three dimensions, with the currently accepted values being $t_{2D} = 1.30(1)$, $t_{3D} = 2.01(2)$, and $T_{2D} = 3.96(4)$ (Zabolitzky et al. 1985). In three-dimensional bond-bending networks, $T_{3D} \approx 3.75$ (Sahimi and Arbabi 1993b), and both of these elastic critical exponents are consistent with the relation $T = t + 2\nu$, which is claimed to be exact (Bergman 2003). Here ν is the percolation critical exponent, and $\nu_{2D} = 4/3$ and $\nu_{3D} = 0.88(1)$. It is worth noting that a model where hard inclusions are placed in a soft elastic background has a different behavior. The critical point is the point at which an infinite hard cluster percolates. On approach to this point from below, the elastic constant diverges $E \sim |\Delta p|^{-s}$. The analogous electrical problem consists of perfectly conducting inclusions in a finite conductivity matrix where $\sigma \sim |\Delta p|^{-s}$. In this case Bergman (Bergman 2003) argues that $s = S$. The lattice results quoted above require modification in the case of continuum systems, for example, in cases where holes are punched randomly in a sheet so that narrow necks of material can exist (Feng et al. 1987). This case is non-universal in both the

conductivity and elasticity cases, though the geometric exponents, such as ν , remain universal.

Elastic percolation on central-force networks occurs at different thresholds than conductivity percolation on the same networks. Maxwell counting gives a good first approximation to the elastic percolation thresholds; however, precise values can only be found by direct simulation. Direct simulations of central-force networks in two and three dimensions have been quite controversial; however, the consensus seems to be that the behavior in two dimensions close to criticality is in the bond-bending universality class described in the paragraph above (Hansen and Roux 1989). However, central-force systems in three dimensions (Sahimi and Arbabi 1993a) exhibit a different behavior, with $T/\nu \approx 2.1$ for body-centered cubic lattices, which is much smaller than the bond-bending value $T/\nu \approx 4.4$. Moreover, the geometry of these systems is now known to exhibit a strong first-order jump (see Fig. 14) in three dimensions (Chubynsky and Thorpe 2007).

The elastic behavior of bond-diluted central-force systems is remarkably simple away from p_r and is well described by a simple linear relation found using effective medium theory (Feng et al. 1985). The critical regime appears to be quite narrow in these central-force models. It is also important to note that the results for p_r found from combinatorial methods apply to triangular lattices where the sites are randomly displaced from their regular locations to remove degeneracies. This may be the reason that geometric calculations of p_r on triangular lattices are higher 0.6603 (Jacobs and Thorpe 1995) than values found from direct solution of elastic response on regular lattices where $p_r \sim 0.64$ (Day et al. 1986). A further complication is that elastic calculations on displaced lattices lead to a nonlinear stiffening of the lattice as bonds which are nearly colinear are brought into alignment by the applied stress and lead to a stiffening of the network (Moukarzel and Duxbury 1995).

In geometric models of rigidity, as described above and in section “Exact Solution on Bethe Lattices,” the rigidity percolation threshold, p_r , lies above the connectivity percolation threshold,

p_c . However, in real materials, there is usually a finite elastic modulus even in the regime $p_c < p < p_r$, which may arise through a variety of different effects. In polymers, proteins, and chalcogenide glasses, the torsional forces are smaller but significant leading to the onset of elasticity at p_c rather than p_r . Moreover, entropic effects may be significant even in ideal central-force systems, so that thermal fluctuations lead to a finite elastic modulus for all $p > p_c$. This has been demonstrated in simple central-force systems such as diluted square, triangular, and cubic lattices (Plischke et al. 1998). This effect is even more pronounced in cross-linked polymeric systems, such as rubber, where entropic rubber elasticity dominates (Barsky and Plischke 1996; de Gennes 1976; Xing et al. 2004). In these systems, the regime $p_c < p < p_r$ is extremely broad so that even heavily cross-linked flexible polymeric systems are in this regime. A further mechanism which leads to a reduction of the percolation threshold from that predicted by geometric rigidity is the presence of tension in the network (Tang and Thorpe 1988) or if the natural length of the springs in the network is taken to zero. Moreover, the elastic critical exponent observed in entropic systems and in systems in tension is usually quite close to the conductivity value, as first predicted by de Gennes in 1976 (Barsky and Plischke 1996; de Gennes 1976; Xing et al. 2004) and as observed in many experiments on gels (see section “Gels and Semiflexible Rod Networks”).

Final Remarks and Future Directions

The relevance of rigidity percolation to granular media and to semiflexible polymer networks is now well established, though many issues remain unresolved. Ideal experiments to test the recent theoretical predictions will greatly clarify the extent to which current rigidity concepts are sufficient to describe these systems. The intermediate phase in chalcogenide glasses is a stimulating, and physically very natural, concept that perhaps could be observed in large-scale molecular dynamics simulations with realistic potentials of systems such as $Se_{1-x}Ge_x$. Presumably there is a

dynamical length scale at which self-organization is possible, which limits the extent of the intermediate phase.

Graph combinatorial methods and direct elastic model simulations provide complementary information about the mechanical response of complex materials. The combinatorial methods however remain limited due to the absence of an exact combinatorial characterization of rigid structures in three-dimensional central-force networks. Moreover, the physical significance of banana configurations, as illustrated in Fig. 11a, remains unexplored and is an intriguing outstanding problem. The common occurrence of a strong first-order jump in the infinite rigid cluster along with a continuous elastic behavior (Chubynsky and Thorpe 2007; Moukarzel and Duxbury 1990; Obukhov 1995) is surprising and also largely unexplored.

Rigidity percolation is emerging as a geometric model for structural glasses (Wyart 2005). Clearly thermal effects are critical in many applications of rigidity percolation so that models which treat both geometric and thermal effects are valuable. Molecular dynamics models provide insight into the interplay of geometry and temperature and warrant further study. In particular the evolution of the Boson peak in model glasses as a function of geometry and temperature remains unexplored and would help resolve contrasting models which emphasize either temperature effects (Parisi 2003) or geometric effects (Wyart 2005).

The role of generic as compared to nongeneric configurations is critical to granular media and to the elasticity of lattices. Even the most basic questions remain unresolved, for example, are the elastic exponents of regular lattices the same as the elastic exponents of random lattices with the same coordination? Is the elasticity of random generic networks inherently nonlinear due to alignment of bonds under stress?

Nevertheless, rigidity percolation provides a useful model for a broad range of physical phenomena, significantly generalizing the connectivity percolation model. Combinatorial methods drawn from graph theory have greatly extended our understanding of rigidity, providing both practical tools and conceptual novelties including

the distinction between generic and nongeneric rigidity. The applications of related geometric methods to granular media and to semiflexible gels are extremely rich and are harbingers of a broader use of rigidity concepts in the analysis of the mechanical behavior of complex materials.

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Networks, Flexibility and Mobility in

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Article Outline

Glossary
Definition of the Subject
Introduction
Flexibility
Maxwell Counting
Enumeration Methods
Molecular Framework Conjecture
Geometrical Simulation
Future Directions
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Glossary

Atypical graph A special graph with symmetry, such as parallel lines – in contrast to a generic graph.

Covalent bond When a covalent bond exists between two atoms in a molecule, the bond length is fixed and independent of the environment. The bond angle is also usually fixed between two covalent bonds that share a common atom.

Dihedral angle rotation A rotation about a covalent bond connecting two atoms in a larger molecule.

Generic graph A graph with arbitrary positions of the vertices and associated edges.

Geometrical simulation A technique that allows the motion of the flexible parts of a network to be determined while obeying all the constraints, both equalities and inequalities.

Graph A set of vertices connected by edges.

Hypostatic When the number of degrees of freedom is less than the number of constraints plus the number of rigid body motions.

Hypostatic When the number of degrees of freedom is greater than the number of constraints plus the number of rigid body motions.

Isostatic When the number of degrees of freedom is equal to the number of constraints plus the number of rigid body motions.

Macromolecule A large number of atoms connected by covalent bonds.

Maxwell count A global estimate of the number of degrees of freedom that assumes that every edge (constraint) is independent.

Molecular dynamics The solution of the classical equations of motion for a system of particles moving under a given potential.

Network glass Non crystalline network made up of atoms that form covalent bonds with each other.

Nuclear magnetic resonance An experimental technique that can be used to probe the different conformational states of a molecule.

Pebble game A procedure for book keeping between degrees of freedom and constraints that allows a rigid region decomposition to be performed on a graph.

Protein A large macromolecule made up of amino acids linked together to form a polypeptide chain, which folds into a compact structure that has a biological function.

Redundant edge An edge that can be removed without changing the rigid regions in the graph.

Rigid region decomposition The division of a graph into rigid regions, both with and without redundant edges, and the flexible regions between them.

Definition of the Subject

A network can be represented by a graph that can be either rigid or flexible depending on the number and distribution of the constraints. A constraint is a length that is fixed. One example of a network is a collection of points in space connected by edges. If the number of edges is large enough and homoge-

neous enough in distribution, then the system is a rigid body, and no motion is possible, except for translations and rotations of the whole network. If a sufficient number of edges are removed, then parts of the systems can become flexible, which means that local motion is possible while maintaining all the constraints. Another manifestation of such a system is a collection of bodies in space connected by bars. Once it is determined that there are flexible parts in the graph, the actual motion, or mobility, can be found. Such graphs were first studied by Maxwell (1864a) in the 1860s using ideas previously developed by Lagrange (1788) in the 1780s. Exact enumeration methods were developed later, starting with Laman (1970) in 1970 for two-dimensional systems and can be extended in three-dimensional graphs in some cases (Whiteley 2005; Chubynsky and Thorpe 2007). The mobility of flexible graphs can be studied using geometrical simulation (Wells et al. 2005).

This general approach, involving flexibility and mobility, has important applications in complex graphs (networks) where it is difficult to solve the classical equations of motion (Goldstein et al. 2002) within a potential energy landscape (Wales 2003), and insight can be gained by approximating the energy landscape by a set of appropriate constraints. These constraints can be either equalities as described above, which are important in determining the flexibility of the network, or equalities augmented by inequalities which determine the subsequent mobility. Two important applications at the atomic and molecular level are network glasses and proteins.

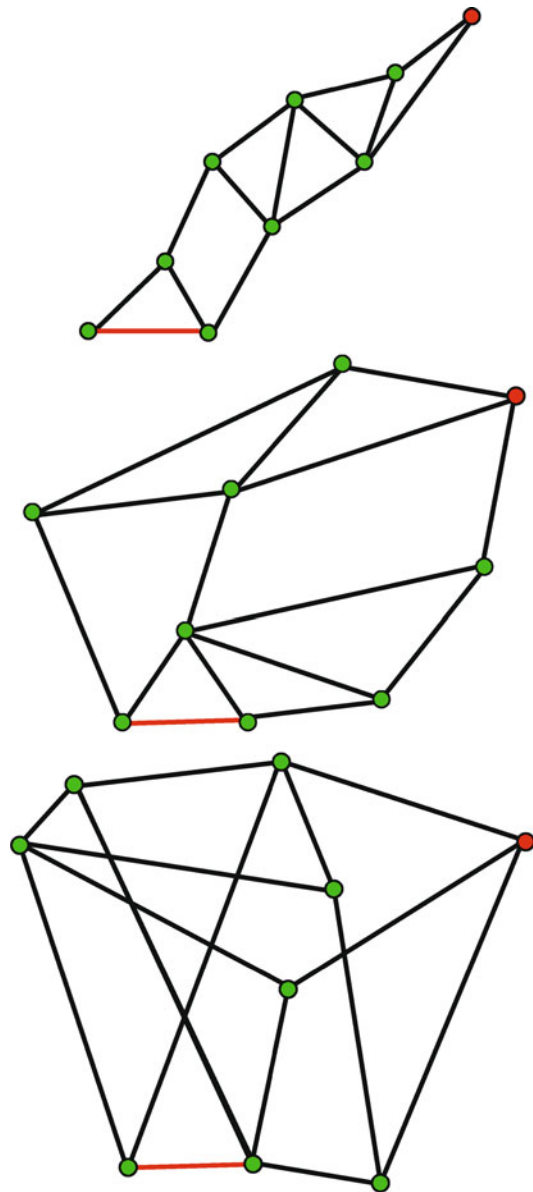
Introduction

As well as developing the famous equations that describe electromagnetism, Maxwell also studied the stability of structures (Maxwell 1864a, b), although this work is very much less well known. He represented a structure, for example a trestle bridge, by a series of vertices and edges, and then estimated whether the structure was stable or not. In two dimensions, a triangle is rigid but a quadrilateral can be deformed as there is one internal degree of freedom. In general the number of degrees of freedom F is given by

$$F = dN - N_c$$

where there are N points embedded in a d dimensional space with N_c constraints, where a constraint is an edge. Examples are given in Fig. 1.

As an introduction, we use popsicle sticks and cotter pins (also called split pins) to construct

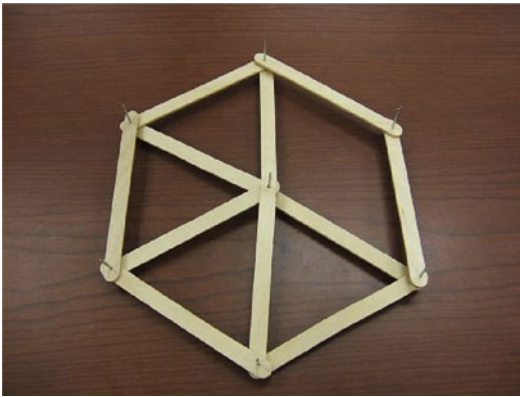


Networks, Flexibility and Mobility in, Fig. 1 Showing three examples of two-dimensional isostatic networks consisting of 9 vertices and 15 edges

framework structures. Each popsicle stick has a small hole drilled near each end, through which the cotter pins can be placed. The pin put through two or more sticks, as shown in Fig. 1, in order to construct a two dimensional framework. A pin allows for possible hinge type motion at the joint, even if the two parts of the split pin are opened. A triangle of popsicle sticks is rigid as no internal deformations are possible, and in a similar way the two edge-sharing popsticks in the upper part of Fig. 2 are rigid.

An individual popsicle stick on a two dimensional surface has 3 degrees of freedom. This can be most easily seen as the two degrees of freedom associated with the center of mass plus a rotation about the center of mass. Thus if there are a total of N_{st} popsicle sticks, then there are initially $3N_{st}$ degrees of freedom (replacing dN in the previous equation) before any cotter pins are added to form joints. When a cotter pin is placed through the holes in two sticks, the holes must be aligned in both the x and y directions, giving two constraints. Each additional popsicle stick added onto a cotter pin, means two additional constraints, so that the total number of constraints is $N_c = 2\sum_r n_r(r-1)$, where there are n_r joints with r popsicle sticks coming together. Thus the number of degrees of freedom can be written as

$$F = 3N_{st} - 2\sum_r n_r(r-1)$$



Networks, Flexibility and Mobility in, Fig. 2 Showing how popsicle sticks and cotter pins can be used to construct framework structures

where it is convenient to let the sum include dangling ends where $r = 1$ in what follows. The total number of sticks is $N_{st} = \sum_r n_r r/2$ and the total number of cotter pins is $N_{cp} = \sum_r n_r$ so that the equation above can be written in the convenient form

$$F = 2N_{cp} - N_{st}.$$

From Fig. 2, we have $N_{st} = 11$ and $N_{cp} = 7$, so that from the equation above, the number of floppy modes $F = 3$. These three are the macroscopic motions of the whole structure (two translations and one rotation) and there are no internal floppy modes. Note that the surprisingly simple formula above applies even if frameworks with unattached popsicle sticks (dangling ends with $r = 1$) are present as long as a cotter pin is placed in the hole of the dangling end. Although such a pin serves no purpose, it does help simplify the counting and leads to the simple equation above.

The approach above needs correction when redundant popsicle sticks are present – for example if the last spoke is included in Fig. 2, then there is a single redundant popsicle stick present and the count needs modifying. Note that removing any one of the 12 popsicle sticks in such a framework will remove the redundancy. The great challenge of rigidity theory is going beyond the simple counts given here to account for redundancy.

The approach taken here focused on the popsicle sticks as the fundamental objects or bodies, and the cotter pins as constraints. However it is often convenient to reverse this and treat the cotter pins as point objects and the popsicle sticks as constraints. The meaning of the equation above now becomes clearer. Each cotter pin has 2 degrees of freedom, as it is a point in a two dimensional plane and so no rotations are involved. This is the origin of the term $2N_{cp}$ and the term N_{st} represents the number of constraints (N_c). Hence in further analysis in two dimensions in this section, we will use the first equation in this section with $d = 2$ to give

$$F = 2N - N_c.$$

An example is given in Fig. 1, where each of the three panels has $d = 2$, $N = 9$ and $N_c = 15$, so

that $F = 3$. These three degrees of freedom are the two translations and the one rotation, associated with the rigid body macroscopic motions of the whole system. This can be thought of in terms of surveying, where the conventional technique using triangulation produces a graph that is made up of a series of edge sharing triangles as shown in the upper left panel. The baseline, together with the distant point to be located with respect to the baseline, are shown in red. This produces an isostatic graph as do the other two panels, although these would probably not be used by any practicing surveyor! Thus, there are no internal motions within these three isostatic networks. This kind of single global count is referred to as the Maxwell count, and is accurate as long as all the counted constraints are independent. The problem of course is that it is hard to know whether constraints are independent or not a priori, especially in very large graphs. Thus, the Maxwell count should be thought of as an estimate or global count, which is good if the network is fairly homogeneous as in the three examples in Fig. 1.

Adding additional edges to the graphs in Fig. 1, leads to redundancy, which is of course very desirable in a building, where one does not want to have the building collapse if a single beam (edge) fails. It also leads to stability against mutations and thermal motions in proteins (Rader et al. 2002). If the number of edges associated with each vertex varies a lot throughout the system, then the Maxwell count is incorrect and may or may not be useful as an estimate. In the examples in Fig. 1, the Maxwell count is exact, and there are just enough connections to hold the system rigid, making all three graphs isostatic. If an edge is removed in any of three graphs, there will be a single internal degree of freedom or floppy mode and the graph is called hypostatic. If an additional edge is added then there is a single redundant edge and the graph is called hyperstatic.

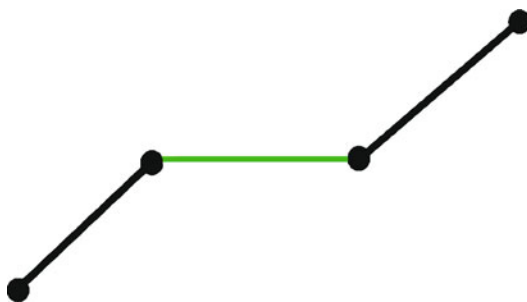
The study of such graphs to determine flexibility does not involve any motion, and so belongs in the realm of statics. That is the knowledge that a region is flexible, determines the potential for motion, but does not determine its amplitude. Here we are dealing with virtual displacements. To study mobility, it is necessary to make actual

displacements and study the motion of the graph. Here an additional set of inequality constraints may be introduced, such that each vertex becomes a hard disc (in two dimensions) or a hard sphere in (three dimensions) where such objects are not allowed to interpenetrate. Such inequality constraints are irrelevant for the static analysis of a graph, but greatly cut down on the mobility of the flexible regions when motion is allowed.

Macromolecules and disordered solids can be represented by graphs, where the atoms are the vertices and the distance between nearest neighbor atoms are the edges. This is particularly appropriate for covalent bonds (Pauling 1928), where the bond length is fixed to within a few percent and the bond angle between adjacent covalent bonds that share a common atom is also fixed similarly and can be represented by an edge connecting second neighbors. The system is still potentially flexible in three dimensions as dihedral angle rotations are allowed, involving a twist along a linear section with four atoms, if no other constraints are present to forbid such motion. This is a three-dimensional example of a hinge and is shown in Fig. 3.

Flexibility

A graph is defined by its vertices and edges, which can be used to represent a physical system like a glass or a protein, where the vertices are atoms. Laman's theorem (1970) in two dimensions can be thought of as a Maxwell count but applied on



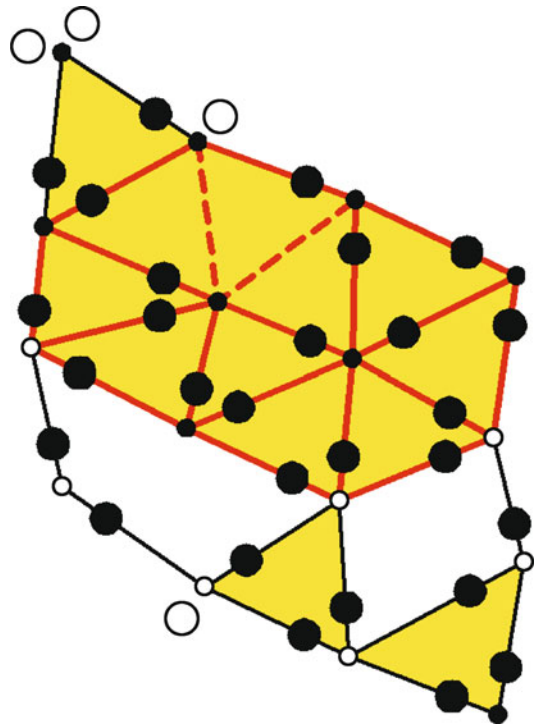
Networks, Flexibility and Mobility in, Fig. 3 Showing a molecular hinge in three dimensions where dihedral angle rotations are allowed using the *green bond* as an axis

all length scales to each subgraph. This is a topological theorem. The Maxwell count is also topological, in that the particular value of the lengths of the edges are irrelevant. Such graphs are called generic and have no special angles or lengths associated with them, and represent the whole class of such graphs. Graphs that do have symmetries like parallel lines, are called atypical and there is no general theory of the flexibility of such graphs although much is known as a result of work by Dove et al. (1995, 1996, 1997, 2000) and Guest (Kangwai and Guest 1999; Fowler and Guest 2002). This is a rare case where the existence of symmetry is not a simplification, but rather a serious complication that can introduce additional degrees of freedom. Alternative methods using group theory appropriate for the symmetry can be used in crystalline lattices (Ashcroft and Mermin 1976) and icosahedral viral capsids (Kangwai and Guest 1999).

Laman's theorem (1970) has been put into an algorithmic form by Hendrickson (1992) and implemented by Jacobs and Thorpe (1995, 1996) and Jacobs and Hendrickson (1997) in an algorithm called the pebble game. In this algorithm, two free pebbles are associated with each vertex in the graph and can be moved onto independent edges in order to maintain the proper book keeping between degrees of freedom and constraints. An example of the output of a pebble game search for a small graph is shown in Fig. 4.

Maxwell Counting

We return now to the global count as first introduced by Maxwell. This is a very simple and useful way to estimate if a network is rigid. Let us consider a regular lattice like a triangular net in two dimensions and a face centered cubic lattice in three dimensions. These must be slightly distorted to make them generic. If we have N sites, each with z neighbors present independently with probability p , then there are dN degrees of freedom and $Nzp/2$ constraints (assumed independent) associated with the bonds between nearest neighbors. Thus, the Maxwell estimate of the number of degrees of freedom is given by



Networks, Flexibility and Mobility in, Fig. 4 Showing the result of a pebble game in two dimensions, where the four free pebbles (*unshaded*) designate the three macroscopic rigid body modes (two translations and one rotation) and the single internal floppy mode, which can be visualized as a rocking of the flower part of the graph

$$F = dN - \frac{Nzp}{2} = dN \left(1 - \frac{\langle r \rangle}{2d} \right)$$

where we define a mean coordination $\langle r \rangle = zp$. This means that the number of floppy modes goes to zero at

$$\langle r \rangle = zp_c = 2d$$

which gives an estimate for the critical fraction of bonds present at rigidity percolation at $p_c = 2d/z$. Of course the Maxwell count fails as the phase transition is approached, and fails catastrophically above the phase transition, where it yields a negative number of floppy modes! This estimate gives $p_c = 2/3$ for the triangular network in two dimensions and $p_c = 1/2$ for the face centered cubic lattice in three dimensions. These estimates are very close to the best current numerical

estimates determined using the pebble game of 0.6602 (Jacobs and Thorpe 1996) and 0.4967 (Chubynsky and Thorpe 2007), respectively. This shows the remarkable accuracy of the Maxwell estimates for rigidity percolation. It is sometimes said that the Maxwell count is a mean field theory, but we prefer to use the term global count (Jacobs and Thorpe 1996). Nevertheless, there are hidden long range effects in rigidity which is reminiscent of mean field theory (Kittel and Shore 1965). Note that the phase transition is second order in two dimensions (Jacobs and Thorpe 1996) but can be first order in three dimensions (Chubynsky and Thorpe 2007), but nevertheless the Maxwell estimates p_c are excellent in both cases. A typical sample of a triangular net very near percolation is shown in Fig. 5.

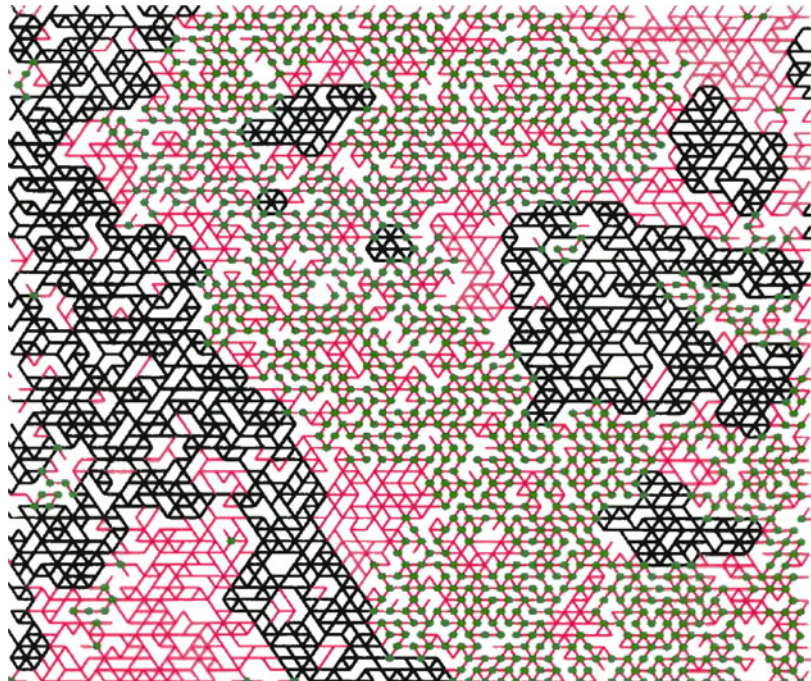
Enumeration Methods

Although the Maxwell count gives a good global picture in many cases, it gives no information about site to site variations. This was accomplished by Laman (1970) in 1970 who showed

how the Maxwell count should be applied to each and every subgraph of the network to get a complete microscopic solution as shown for example in Fig. 5. Laman's theorem was turned into an algorithm by Hendrikson (1992) that has been implemented on the computer by Jacobs and Thorpe (1995, 1996). This leads to the rigid region decomposition of the kind shown in Fig. 5. This ability to examine very large networks with 100,000 atoms and more and to obtain a rather complete description of the second-order phase transition for the triangular net and the associated geometrical critical exponents (Jacobs and Thorpe 1996; Arbabi and Sahimi 1993) is extremely useful. Response functions, like elastic constants can also be calculated, but much less accurately as more traditional approaches like conjugate gradient methods must be used on smaller lattices (Feng et al. 1985). The elastic constants go to zero as the phase transition is approached from the rigid side for bond dilution on both the triangular lattice and the face-centered cubic lattice (Feng et al. 1985) which is surprising as the phase transition for the face-centered cubic lattice is first order. This result requires further explanation.

Networks, Flexibility and Mobility in,

Fig. 5 Showing a piece of a triangular network very near percolation, caused by bond dilution. Hinges are shown in *green*, isostatic regions in *red* and hyperstatic regions in *black*



Molecular Framework Conjecture

Rigidity in three dimensions is much more complicated than in two dimensions because of the existence of “banana diagrams”, an example of which is shown in Fig. 6. The three rigid yellow pieces are the bananas and it can be seen that these can rotate as indicated by the arrows. The complication is that the three green sites themselves form a non-contiguous rigid cluster. This cannot happen in two dimensions (see Figs. 4 and 5), where all the individual rigid clusters are contiguous and represent a major complication. It means that there is no Laman-type theorem and hence no pebble game. Nevertheless, a very accurate, but approximate, pebble game has been developed for general three-dimensional networks (Chubynsky and Thorpe 2007) that for example is estimated to be accurate to 1 part in 10^9 for bond diluted face-centered cubic lattices.

There is one very important special case in three dimensions, which is the bond-bending network, where there are angular forces associated every each pair of central forces that share a common vertex. These angular forces can be thought of as second neighbor central forces. For these special networks there is a conjecture; called the

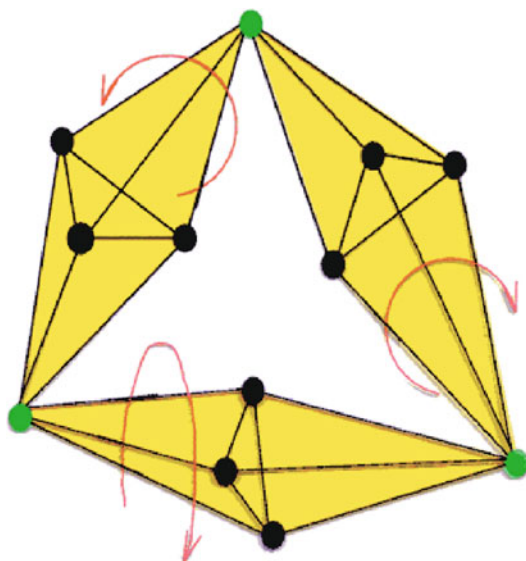
Molecular Framework Conjecture that the appropriate pebble game is exact (Whiteley 2005, 1999; Tay and Whiteley 2005). This is a very fortunate situation as this is the case of most practical interest. Examples of such molecular frameworks are covalent glasses like GeAsSe as shown in Fig. 7, where the coloring of the sites reflects the chemistry (dark blue for 4-coordinated Ge, light blue for 3-coordinated As and yellow for 20-coordinated Se), and the bond coloring reflects whether they are flexible (green), rigid (red) or stressed and rigid (black).

Maxwell counting can be used to estimate when these networks undergo a transition from rigid to flexible. If there are n_r sites with r -coordinated atoms, where r is 2, 3 or 4, then the total number of atoms $N = \sum_r n_r$ and the mean coordination $\langle r \rangle = \sum_r r n_r / N$. The total number of degrees of freedom is $3N$. The number of angular constraints is $r/2$ for central forces and $3r - 5$ for angular forces, both associated with an r -coordinated site. Therefore, the number of floppy modes is

$$F = 3N - \sum_r n_r \left[\frac{r}{2} + (2r - 3) \right] \\ = 6N \left[1 - 5 \frac{\langle r \rangle}{12} \right]$$

which gives a phase transition from rigid to flexible when $\langle r \rangle = 12/5 = 2.4$ (Phillips 1979; Thorpe 1983; He and Thorpe 1985). Note that reference (Phillips 1979) which first applied these counting ideas to network glasses, contains an error as six angular constraints rather than the correct five independent angular constraints were assigned to a 4-coordinated site. Exact enumerations, using the pebble game on computer generated networks give $\langle r \rangle = 2.385$ for the location of the phase transition (Thorpe et al. 1999). Thus, when the polymer chains made up of 2-coordinated atoms are lightly cross-linked, the network is flexible, but as the number of cross-links becomes quite dense and the mean coordination rises to around 2.4, the network becomes rigid (Thorpe 1983).

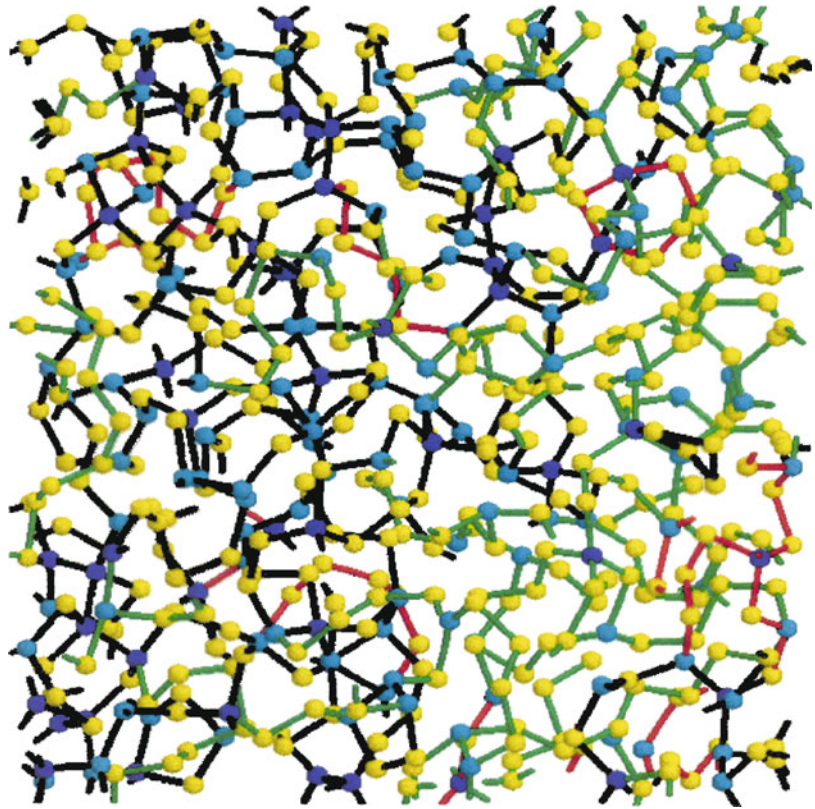
The molecular framework conjecture also applies to proteins, which are large macromolecules containing many hundreds of atoms.



Networks, Flexibility and Mobility in, Fig. 6 Showing the problematic banana diagram in three dimensions

Networks, Flexibility and Mobility in,

Fig. 7 Showing a piece of a covalent glass near the phase transition at a mean coordination $\langle r \rangle = 2.4$, where the *green bonds* are hinges, the *red bonds* isostatic and the *black bonds* hyperstatic



Proteins are polypeptide chains that are crossed linked by hydrophobic tethers and hydrogen bonds to form rather compact three-dimensional structures (Jacobs et al. 2001). A rigid region decomposition of a typical protein, barnase is shown in Fig. 8.

Proteins have enough rigidity to define their threedimensional structure, while retaining sufficient flexibility to function. Thus, they exist in a narrow window around the phase transition between flexible and rigid (Rader et al. 2002). This is shown in Fig. 9, which also shows that covalent glasses behave in a very similar way.

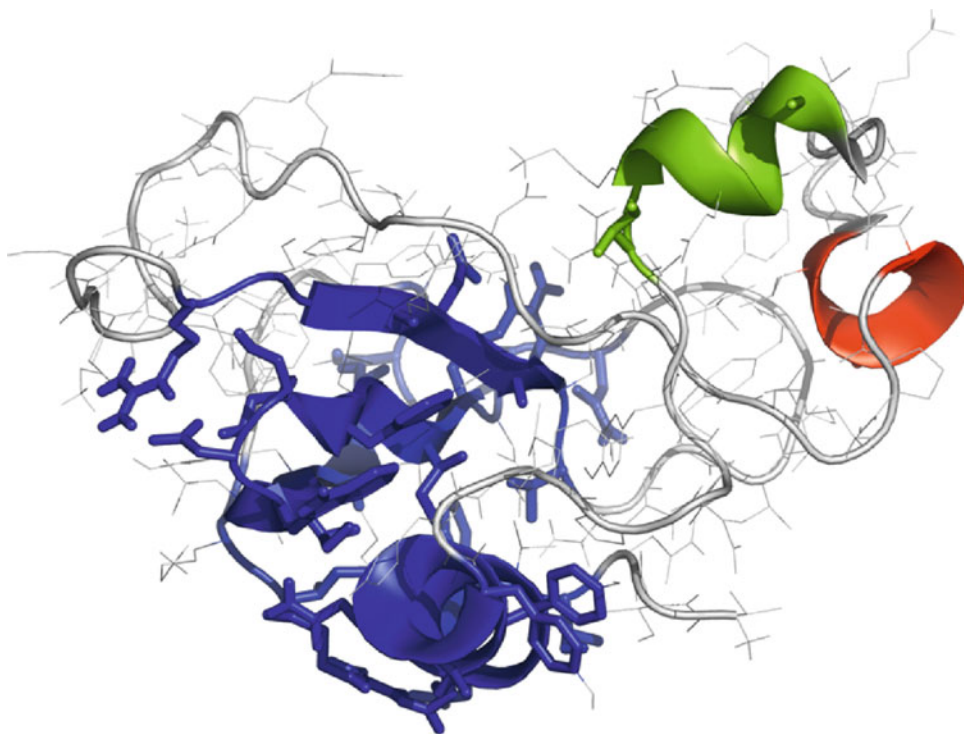
Geometrical Simulation

The approach described here comes from an area of mathematics called rigidity theory, which yields powerful results without much calculational or computational overhead. However, these results are limited as no actual motion is involved, and it is only the possibility of motion,

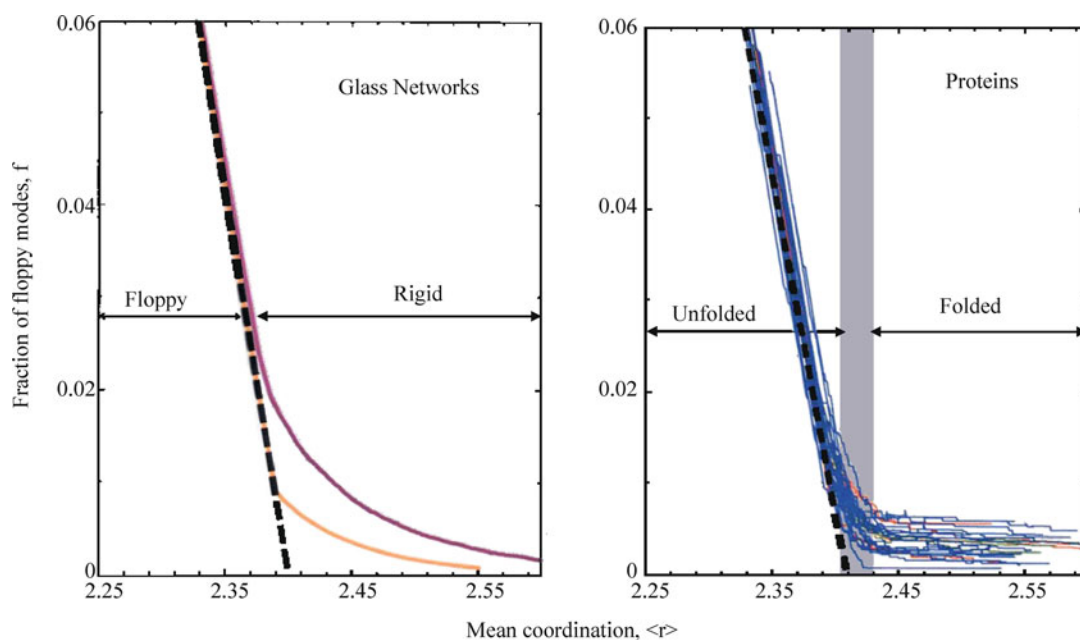
or absence of motion, that is addressed. This is very valuable information.

However, for a more complete description, it is desirable to know the mobility, or the amplitudes of the motion, which do not violate any of the original constraints. In addition, the motion may involve additional constraints, the most important being inequalities that prevent objects from interpenetrating. For example, two-dimensions discs are not allowed to overlap, and in three dimensions, spheres are prevented from interpenetrating. An example is shown in Fig. 10, where the vertices from the lower panel in Fig. 1 have been replaced by discs of various radii.

Pairs of discs are not allowed to overlap during the motion. As the disc radii are increased, the amplitude of the floppy mode is liable to be decreased, by the necessity to avoid collisions. Geometric simulation methods can be used to study such motion (Lei et al. 2004; Lee et al. 2005; Wells et al. 2005) and these are rather efficient. Key ingredients are the introduction of



Networks, Flexibility and Mobility in, Fig. 8 Showing a piece of the protein barnase with the three largest rigid regions picked out in the three different *solid colors*

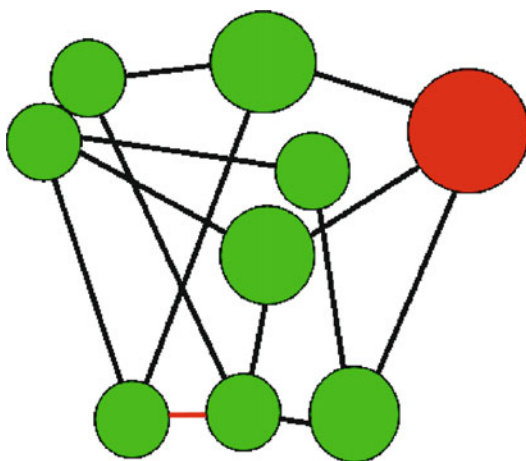


Networks, Flexibility and Mobility in, Fig. 9 Showing the similar behavior of the number of floppy modes in covalent network glasses and a selection of proteins (Rader et al. 2002). In all cases the transition from flexible

to rigid occurs around a mean coordination $\langle r \rangle = 2.4$. Here $f = F/3N$ is the number of floppy modes per degree of freedom

random or directed small displacements, the maintenance of constraints and collision avoidance. The reader is referred to the articles above for more details.

Geometrical simulation techniques are similar in three dimensions, and for example new conformations of molecules can be generated. An example is shown in Fig. 11 for the protein barnase, previously shown in Fig. 8. A set of 20 conformers obtained from a nuclear magnetic resonance experiment (Bycroft et al. 1991) are shown in the left panel. These are determined from experiments where a sufficient number of constraints are determined that the remaining indeterminacy is



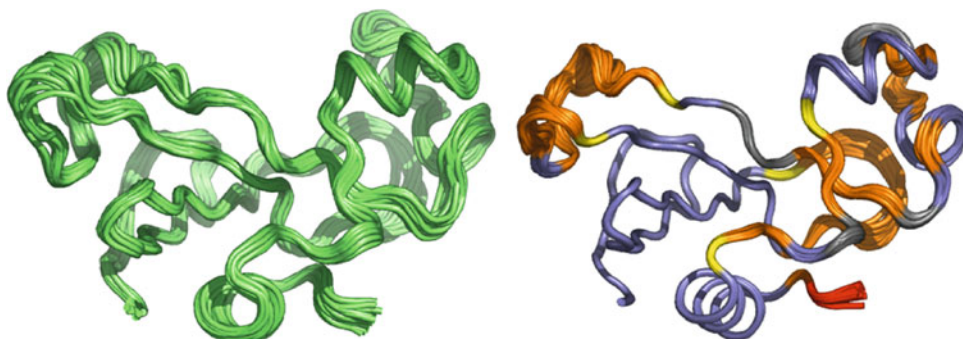
Networks, Flexibility and Mobility in, Fig. 10 Showing the two-dimensional graph from the lower panel in Fig. 1, with a single edge removed, so that the graph becomes hypostatic with a single floppy mode

associated with the protein mobility. In the right panel, a single X-ray structure (Hartley 1989) is used as a starting point to generate many new protein conformations consistent with the constraints. The 20 simulation conformers shown are selected from a much larger set and are spaced well apart (Wells et al. 2005). The blue regions in the left panel are rigid, and the other regions are flexible, leading to mobility. Note that distinct rigid regions can move with respect to other rigid regions.

A quantitative comparison between the Root Mean Square Distance (RMSD) and the residue number between the nuclear magnetic resonance experiment and the geometric simulations is shown in Fig. 12. The amplitudes obtained from both the experiment and from geometrical simulation are absolute, so no scaling is required. The residue number refers to the numbering of the amino acids along the backbone of the polypeptide chain that folds to produce the three-dimensional protein structure.

Future Directions

In this brief article, we have set down the key ingredients that are needed when considering the flexibility and mobility of networks, with an emphasis on the important class of three-dimensional molecular networks. For more details of the more mathematical aspects of the theory of rigidity, the reader is referred first to the books

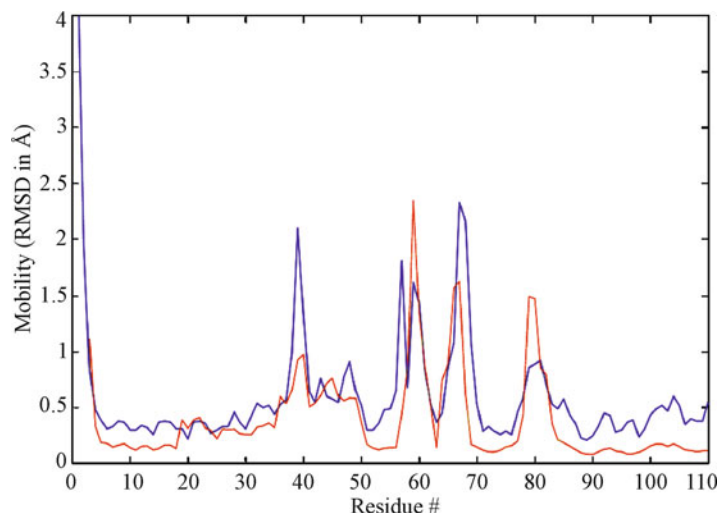


Networks, Flexibility and Mobility in, Fig. 11 Showing a comparison between the NMR ensemble of conformers (*left*) for barnase and the set of

conformers (*right*) generated using geometrical simulation techniques from a single X-ray crystallographic structure (Wells et al. 2005)

Networks, Flexibility and Mobility in,

Fig. 12 Plotting the mobility of each residue, as determined using experimental data (blue) from Fig. 11, and showing that geometric simulation (red) captures the main features of the mobility of the protein, when compared with nuclear magnetic resonance data (Wells et al. 2005)



referenced at the end. There are few review articles in this area as these approaches are quite new and are still being developed.

The static part of rigidity has led to an exact theorem (Laman 1970) and fast algorithms in two dimensions (Jacobs and Thorpe 1995, 1996; Jacobs and Hendrickson 1997). There is no theorem in three dimensions for the general case, although there is the special case of the very useful molecular framework conjecture (Whiteley 2005) that remains to be proved. Algorithms have been developed recently based on the molecular framework conjecture (Thorpe et al. 1999; Jacobs et al. 1999, 2001; Jacobs 1998; Hespeneide et al. 2004). Although there is no theorem or conjecture for the general case in three dimensions, approximate, but rather accurate, algorithms nevertheless have been developed (Chubynsky and Thorpe 2007). There is a need for a more complete description of the unique features of rigidity in three dimensions, associated with banana diagrams etc. At this time there seems no great motivation for studying rigidity in dimensions higher than three.

Geometrical simulation is still in its infancy – this is a more complex problem than the movement of robot arms (Streinu 2000) because many interlocking rings of constraints are involved and the environment is crowded in general. This is rather like moving groups of friends holding hands tightly in rings through a football crowd at

the end of a game. Early efforts focused on ring closure (Lei et al. 2004; Kuhn et al. 2004), but these proved inefficient and have been largely abandoned in favor of small Monte Carlo-type moves that initially violate the constraints, followed by various guiding and shaking procedures to restore the constraints and arrive at a new conformation (Wells et al. 2005). The inequalities associated with the van der Waals or hard sphere overlaps cause particular concern in the crowded molecular environments found in proteins and better ways of handling this are needed. Ultimately the results of such approaches, obtained rapidly, can be used as input with phenomenological classical potentials (McCammon et al. 1977) of the kind used in molecular dynamics (Brooks et al. 1983; Pearlman et al. 1995), to be able to generate larger amplitude motions for a given amount of computer time.

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Percolation and Polymer Morphology and Rheology

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Article Outline

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Bibliography

Glossary

Branched polymers Large polymers below the gel point with radii larger than the correlation length.

Chemical gels Gel networks in which the monomers are covalently bonded.

Critical gels The gel networks at the gel point.

Elastic networks Networks in which each bond is an elastic element, such as a Hookean spring.

Gel point The point at which the critical gel network is formed for the first time.

Lattice animals Large percolation clusters below the percolation threshold with radii larger than the correlation length.

Physical gels Gel networks in which the monomers or particles are connected through weak association.

Relaxation time spectrum The distribution of relaxation times that describes the linear viscoelastic behavior of liquids and solids.

Resistor networks Networks in which each bond is a resistor with a given conductivity.

Rigidity percolation Percolation networks in which each uncut bond is a Hookean spring, and there are no angle-changing forces.

Sol The solvent + finite polymer clusters below the gel point.

Definition of the Subject and Its Importance

Elastic percolation networks described in the chapter ► [“Elastic Percolation Networks”](#) by Duxbury (see also below), random resistor networks described in the articles by Hughes and Balberg, and a few other models (Sahimi 2003) of heterogeneous materials provide a comprehensive understanding of their fundamental properties. The purpose of this chapter is to describe and discuss applications of such percolation models to predicting the structure and rheology of an important class of disordered materials, namely, polymers and gel networks, and test their validity by comparing their predictions with the relevant experimental data.

The formation and structure of the polymeric materials that we consider in this chapter are characterized by the existence of a percolation-like transition point. The rigidity and linear elastic properties of disordered materials, including polymers, that are far from their percolation threshold are well-described and predicted by mean-field theories, such as the effective-medium approximation (Kirkpatrick 1973; Feng et al. 1985). However, the predictions of such theories for effective properties of polymeric materials that are near the percolation threshold deviate greatly from the experimental data. The description of

various properties of such polymeric materials near the percolation threshold is best done by the percolation models, which is the focus of this chapter.

Introduction

Polymeric materials have wide applications in many branches of science and technology. In addition, they have many interesting, and in many cases unusual, properties that justify their study. One is that their relaxation modes are described by a wide spectrum, which provides clues to their structure. Each mode is associated with a particular “event” or motion. In particular, motion of clusters of monomers or molecules is associated with the long modes, with the longest relaxation modes being due to the very large clusters. Such clusters are formed either by the formation of *chemical bonds* or *chemical crosslinking* between the monomers, as well as between the monomers and small molecules or clusters that, when large enough, lead to *phase separation*, or by *physical association* at the molecular or particulate level. It is the formation of such large clusters that is the root cause of an important class of phase transitions, namely, the *liquid-solid transition* (LST), which is a key process in daily life.

The significance of the LST cannot be over-emphasized, as it occurs in a wide variety of problems of practical importance. At the most basic level, it is important to be able to predict the point at which the LST occurs. The knowledge is also necessary for designing better polymer processing operations. An example is injection molding of semicrystalline polymers, the quality of the surface of which is a strong function of the location of the LST point. In other applications, knowledge of the LST point is necessary in order to *postpone* or *avoid* it altogether. Since near the LST point the system is a mixture of solid clusters and a liquid, one may be able to design a wide variety of materials by changing the volume fraction of each phase, which is why study of the LST is important. At the same time, cross-linked polymers near the LST point are good adhesives, and

have also been used as materials for membranes, absorbers, and many other applications.

In addition to chemists and chemical and polymer engineers who have traditionally studied polymers and their properties, a seminal work in the early 1970s attracted the attention of physicists, and opened the way to the application of modern of statistical mechanics to the study of polymers, de Gennes (1972) demonstrated that there is a close connection between linear polymers – those in which the monomers have functionality or coordination number $Z = 2$ – and a statistical mechanical model, namely, the n -vector model. Clearly, no two monomers occupy the same point in space. If, in addition, there is no closed loop in the structure of the polymer, then, the result is a *linear polymer* that, as de Gennes showed, corresponds to the limit $n \rightarrow 0$ of the n -vector model. The most suitable model for such polymers is the path of a self-avoiding walk in which a particle performs a random walk in space with the restriction that it never visits any point more than once, so that loop formation is avoided (Hughes 1995). de Gennes’ discovery made it possible to apply modern methods of statistical mechanics, and in particular the renormalization group theory and the scaling concepts, to the study of linear polymers and, later, to branched polymers and gels.

The original work of de Gennes was restricted to linear polymers. However, if the monomers have functionalities $Z > 2$, so that each of them may be connected with more than two neighboring monomers, then at least two other classes of polymers can be obtained:

- (i) If the reaction time t is relatively short and below, but close to, a characteristic time t_g , then one obtains branched polymers in the solution, usually called the *sol*, which represent a viscous solution. It is called a *sol* because it is soluble in good solvents. Such branched polymers are large but finite clusters of monomers. t_g is called the *gelation time*.
- (ii) If, however, the reaction time is larger than t_g , an infinitely large solid network of reacted and connected monomers appears, which is

usually called a *chemical gel*, or simply a gel. Clearly, as one passes from the sol to the gel phase, there is an LST. This process, called *gelation*, has been described by percolation models.

The gel can only swell, but not dissolve, in a solvent, even if finite clusters of connected monomers still exist in the system. The point at which the gel network appears for the first time – which is, in fact, the point that signals the LST – is called the *gel point* (GP).

The gel network has interesting structural, mechanical, and rheological properties which are described in this chapter. Most of us are already familiar with such sol-gel transformations in our daily lives, since we all know about milk-to-cheese transition, pudding, gelatine, etc. In fact, materials that contain gels, or use their specific properties, are numerous. In addition to the aforementioned examples, another important example is the eye humor. Gels also play an important role in laboratory technology, such as gel chromatography; in the fabrication of a wide variety of products, such as glues, cosmetics, and contact lenses, and in food technology. In addition, the sol-gel transition is a general phenomenon that has been utilized for producing a variety of ceramic materials (Brinker and Scherer 1990). Finally, sol-gel processes are also used for fabrication of nanoparticles for use in novel therapy (Ficai and Grumezescu 2017).

Chemical reactions are responsible for the interconnectivity of the monomers in chemical gels. In general, there are three types of chemical gelation:

- (i) *Poly condensation* (Fakirov 2017) in which polymerization begins with either bifunctional units A-A or trifunctional ones B₃, or more generally Z-functional units B_Z. The A units are linked with the B units, with each elementary reaction being accompanied by the elimination of a molecule between units of A and B. Thus, a polymer network is formed in which the polymer chains are terminated by either A or B. No two units of the same class can participate in a reaction

with each other and, therefore, there is always exactly *one* bifunctional unit between polyfunctional units in the polymer network.

- (ii) *Vulcanization* (Coran 2013) begins with long linear polymer chains in a solution. The chains are then cross-linked by small units. An example is rubber, the elasticity of which is due to the introduction of the S-S bonds between polyisoprene chains. Only a small number of bonds are needed to cross-link the chains and form an interconnected polymer network.

de Gennes (1977) argued that there exists only a very narrow region near the GP in which the percolation model may be applicable to vulcanizing polymers – those with high molecular weights. In other words, such polymers exhibit the type of behavior and physical properties that are well described by the Flory-Stockmayer theory (Flory 1941; Stockmayer 1943), which is a mean-field theory. For this reason, we ignore vulcanization in this chapter.

- (iii) *Additive polymerization* is similar to polycondensation. The initial solution contains two types of units. The A = A units that are bifunctional when the double bond opens, and the B = D = B units that are quadrifunctional when the two double bonds open independently of each other. If the reaction polymerizes A = A units, one obtains A-A-A-A-... chains, whereas a reaction between the A units and the B = D = B units reticulates the network. The length of the chains between two reticulation points is not fixed, but depends crucially on the initiation process and on the relative concentrations of the bi- and quadrifunctional units.

In addition to such chemical gels, one may also have *physical gels* in which the monomers or particles are attached to each other by relatively weak and *reversible* association or by such physical processes as entanglement. A well-known example is silica aerogel (Gurav et al. 2010), which has many applications. Another example is a solution of gelatin in water below a certain critical temperature where a coil-to-helix

transition takes place, and bonds appear to form by winding of helices of two adjacent chains. Such physical gels can be made and also destroyed by thermal treatment. Other important examples include liquid crystalline polymers at their nematic-to-smectic transition, suspensions and emulsions at the percolation threshold, partially crystalline polymers, and microphase-separating block copolymers.

In this chapter we describe modeling of structural, mechanical, and viscoelastic properties of the sol and gel phases, especially near the GP. Modeling of formation of gel networks was pioneered by Flory (1941) and Stockmayer (1943), whose theory is essentially equivalent to percolation on the Bethe lattice, an endlessly branching network without any closed loops. Stauffer (1976) and de Gennes (1976) emphasized the importance of the deviations from the solution of Flory and Stockmayer, and proposed to replace it by percolation on three-dimensional (3D) lattices. This aspect of the problem, which can be described by a percolation model or a variant of it, is now well-understood.

de Gennes (1976) also proposed that the elastic and viscoelastic properties of gel and sol phases can be described by appropriate random resistor network models (see below). His suggestion was widely accepted for a long time, and was utilized for interpreting the experimental data. It was recognized in the 1980s that, while de Gennes' suggestion may be applicable to certain classes of polymeric materials, more general models are needed for several other important classes of such materials. This realization motivated the development of the elastic percolation models that are described in the chapter ► [“Elastic Percolation Networks”](#) by Duxbury. We shall come back to this point shortly.

Percolation Models of Polymerization and Gelation

To understand the connection between the sol-gel transition and the percolation model, consider a solution of molecules or monomers with functionality $Z \geq 3$. Suppose, for simplicity, that the monomers occupy the sites of a periodic lattice.

With probability p , two nearest-neighbor monomers (sites) react and form a chemical bond between them. If p is small, only small polymers – clusters of reacted and connected monomers – are formed. As p increases, increasingly larger polymers with a broad size distribution are formed. The mixture of clusters of connected monomers and the isolated unreacted monomers represents the sol phase. For $p > p_c$, where p_c a characteristic of the lattice that depends on the functionality Z – the number of nearest neighbors of a monomer in the lattice – an infinite cluster of reacted and connected monomers is formed that represents the aforementioned gel network, which at the GP is usually called the *critical gel*. Near the GP the gel usually coexists with the sol such that the finite polymers are trapped in the interior of the gel. For $p \rightarrow 1$, almost all the monomers have reacted and are connected, and the sol phase disappears completely. Thus, p_c signals a *connectivity* transition: For $p > p_c$, an infinite cluster – the gel network – together with (possibly) a few finite-size clusters, exists and, thus, the system is mainly a rigid gel. The fraction of the chemical bonds formed at the GP, which is related to the fraction of the reacted monomers at the GP, is obviously the analogue of the bond percolation threshold. Thus, it should be clear that the formation of branched polymers and gels is very similar to, if not identical with, a percolation process.

In the early days of modeling the sol-gel transition, it was generally assumed that the properties of the polymeric materials at the GP are independent of their structural details. But, despite decades of research, this is still an unproven hypothesis for the critical gel. In addition, the monomers do not react randomly, as there are usually some correlations in the way the monomers react and connect with one another.

Structural Properties of Branched Polymers and Gels

Studies of the sol-gel transition usually proceed by measuring the dynamic evolution of the rheological (e.g., the viscosity) or mechanical properties (e.g., the elastic moduli) during the chemical reaction that leads to gelation, assuming that the experimental parameter – time or frequency – and

the theoretical one – the number of crosslinks – are linearly related to each other in the vicinity of the GP. If true, then, near the GP, $|p - p_c|$ is a measure of the distance from the GP. All the properties of nearly critical gels, that is, those that are very near the GP, can be expanded in powers of $|p - p_c|$, which is similar to, for example, the vapor-liquid phase transition for which all the properties of the system near the critical temperature T_c is expanded in powers of $|T - T_c|$. But, as the distance from the GP increases, the expansions break down.

Rheological measurements usually use a cone-and-plate rheometer, or the more accurate magnetic sphere rheometer. The ranges of shear rates, deformations, and times of measurements in such devices allow the determination of steady-state zero-shear viscosity and steady-state linear elastic moduli up to the vicinity of the LST at the GP, but it has proven to be almost impossible to do such measurements *at* the GP; see below.

The correlation or connectivity length ξ , which represents the typical size of the branched polymers below p_c , diverges as p_c is approached according to the power law

$$\xi \sim |p - p_c|^{-\nu}, \quad (1)$$

which is completely similar to ξ_p , the correlation length of percolation clusters. Below p_c , however, polymers with radii much larger than ξ have completely different characteristics than those with a typical radius ξ . Therefore, we describe and discuss such polymers separately, and refer to them as the *branched polymers* to distinguish them from gel networks. Above the GP the correlation length of the polymers is taken as the mesh size of the gel network. For any length scale greater than ξ the gel network is macroscopically homogeneous.

Scaling Properties of the Morphology of Nearly Critical Gels

Several important structural properties of branched polymers and gel networks can be measured directly or indirectly. The *gel fraction* $f_g(p)$ is the fraction of the monomers that are in the gel network, and is measured by simply weighing the

gel at various times during the polymerization process. Clearly, $f_g(p) > 0$ only if $p > p_c$. As far as the analogy with the percolation model is concerned, f_g is the analogue of percolation fraction or percolation probability $P(p)$ (see the chapter ► “[Percolation Phase Transition](#)” by Sahimi). Of particular interest to us is the behavior of $f_g(p)$ near p_c . In this region,

$$f_g(p) \propto (p - p_c)^\beta. \quad (2)$$

The number distribution of the polymers, that is, the probability $Q(s, \epsilon)$ that a polymer in the sol phase contains s monomers at a distance $\epsilon = |p - p_c|$ from the GP, is the analogue of the cluster-size distribution n_s in the percolation problem (see the chapter ► “[Percolation Phase Transition](#)” by Sahimi). Thus, we may write

$$Q(s, \epsilon) \sim s^{-\tau} h_1(\epsilon s^\sigma), \quad (3)$$

where h_1 is a universal scaling function. Instead of writing the distribution in terms of s , we may write down a power law for the cluster *mass distribution*, $N(M)$, in terms of the molecular weight M of the finite polymers. At the GP, one has

$$N(M) \propto M^{-\tau}, \quad p = p_c \quad (4)$$

Then, near the GP, one has

$$N(M) \propto M^{-\tau} h_2(M/M_z), \quad (5)$$

which is completely similar to Eq. (3), where h_2 is another scaling function, closely related to h_1 .

Using $Q(s, \epsilon)$, we define two distinct mass averages. One, the *weight-average molecular weight*, is defined by

$$M_w = \frac{\int s^2 Q(s, \epsilon) ds}{\int s Q(s, \epsilon) ds} \sim |p - p_c|^{-\gamma}, \quad (6)$$

where $\gamma + 2\beta = \nu d$, with d being the dimensionality of the material. In the analogy with the percolation model, M_w is the analogue of the mean-cluster size (see the chapter ► “[Scaling Theory of Percolation Clusters](#)” by Stauffer and Sahimi).

In the polymer literature M_w is also called the *degree of polymerization*. The second mass average is defined by

$$M_z = \frac{\int s^3 Q(s, \epsilon) ds}{\int s^2 Q(s, \epsilon) ds} \sim \epsilon^{-1/\sigma} \sim |p - p_c|^{-1/\sigma}, \quad (7)$$

where M_z is the same quantity as in Eq. (5) and, $\sigma = (\tau - 2)/\beta$. Note, however, that the average

$$\langle M \rangle = \frac{\int s Q(s, \epsilon) ds}{\int Q(s, \epsilon) ds}$$

does *not* diverge at the GP. Note also that we may also express M_w in terms of ξ :

$$M_w \propto \xi^{\gamma/\nu}. \quad (8)$$

Recall (see the chapter ► “Scaling Theory of Percolation Clusters” by Stauffer and Sahimi) that percolation theory predicts that for 3D systems, $\nu \simeq 0.89$, $\beta \simeq 0.41$, $\tau \simeq 2.18$, $\sigma \simeq 0.46$, and $\gamma \simeq 1.82$. The mean-held theory of Flory and Stockmayer predicts the same power laws, but with, $\beta = \gamma = 1$, $\nu = \sigma = 1/2$, and $\tau = 5/2$.

At the GP the gel network is *not* homogeneous, but is a self-similar fractal object with a fractal dimension D_f that in d -dimensions is given by

$$D_f = d - \beta/\nu = d(\tau - 1)^{-1}, \quad (9)$$

Using numerical estimates of ν and β for the 3D percolation model, we obtain, $D_f \simeq 2.53$. On the other hand, the Flory-Stockmayer theory predicts that, $D_f = 4$, which is unphysical since D_f cannot be larger than 3.

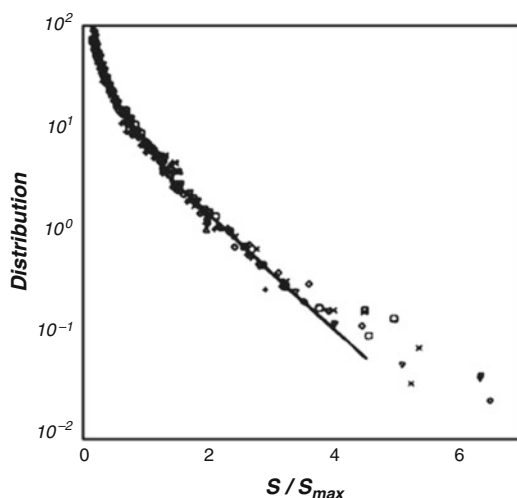
Comparison of Experimental Data with the Percolation Model

Since a main prediction of percolation theory is the existence of universal critical exponents and the fractal dimension D_f and because the numerical value of any polymer property, such as its average molecular weight or the location of the GP, is not universal and depends on the structure

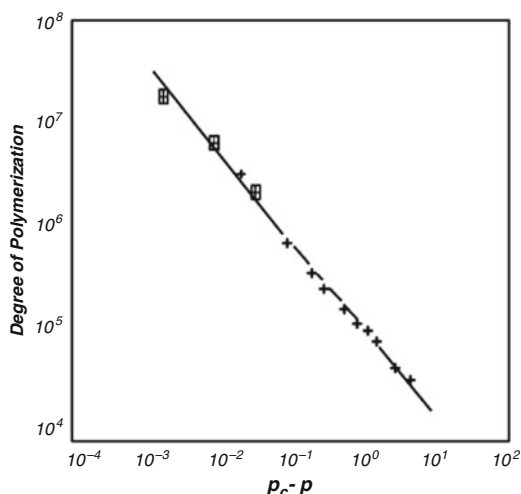
of the polymer, we focus on a comparison between the measured exponents, such as β , γ , and σ , and the predictions of the percolation model.

In their experiments with irradiated polystyrene solution in cyclopentane, Leibler and Schosseler (1985) coupled gel permeation chromatography and light scattering to deduce the polymer size distribution, which provides a direct means of measuring the exponent τ . Figure 1 presents their measurements from which one obtains, $\tau \simeq 2.3 \pm 0.1$, close to the prediction of the percolation model, 2.18. Lapp et al. (1989) further checked this result by carrying out similar experiments in a system made by chemical end-linking of polydimethylsiloxane, and Patton et al. (1989) carried out experiments in a system in which polyester was made by bulk condensation polymerization. The measurements of both groups were consistent with the value of τ predicted by the percolation model.

Adam et al. (1987) tested the validity of the percolation model based on Eq. (6) by carrying out static light scattering measurements on a polyurethane sol. Candau et al. (1985) performed their experiments on polystyrene systems cross-linked with divinylbenzene. Figure 2 displays the results of Adam et al. (1987) from which one obtains



Percolation and Polymer Morphology and Rheology, Fig. 1 Normalized polymer size distribution as a function of polymer size s . Percolation theory predicts the slope to be $1 - \tau \simeq -1.3 \pm 0.1$. (After Leibler and Schossler 1985)



Percolation and Polymer Morphology and Rheology, Fig. 2 Dependence of degree of polymerization M_w on $p_c - p$ for a polyurethane sol. The slope of the curve is $-\gamma_p$. (After Adam et al. 1987)

$\gamma \simeq 1.71 \pm 0.06$, only 5% smaller than the prediction of the percolation model, 1.82. A similar estimate of γ was reported by Candau et al. (1985).

On the other hand, one can also express the weight-average molecular weight in terms of the gel fraction near the GP, $M_w \sim f_g^{-\gamma/\beta}$, thus, a plot of $\log(M_w)$ versus $\log(f_g)$ yields an estimate of γ/β . Schmidt and Burchard (1981) carried out anionic copolymerization of divinylbenzene with styrene and obtained both branched polymers (see below) and gels. Light scattering was used to measure the various properties of interest. When Schmidt and Burchard (1981) plotted $\log(M_w)$ versus $\log(f_g)$, they obtained a straight line with the slope, $\gamma/\beta \simeq 4.5$, in good agreement with the prediction of the percolation model, $\gamma/\beta \simeq 4.44$.

Branched Polymers

After a polymer is formed by crosslinking, the experimentalist usually analyzes its morphology by diluting it in a good solvent. As mentioned above, branched polymers in a dilute solution of a good solvent may swell and have a radius *larger* than their extent at the end of the crosslinking. Thus, it is important to consider both the typical

polymers, which we described in the last section, and the swollen ones that we now consider.

Thus, consider a swollen branched polymer in a good solvent with a radius larger than the polymer correlation length ξ . The structural properties of such branched polymers are described by *lattice animals*, which are, in fact, very large percolation clusters *below* the percolation threshold. Their radii are *larger* than the percolation correlation length ξ_p . But, the interesting and important point is that, although lattice animals are simply very large percolation clusters below p_c , their statistics are completely *different* from those of percolation clusters.

Statistics of Lattice Animals

To better understand the difference between percolation clusters and lattice animals, let us first define a few key statistics of the latter. Suppose that $A_s(p)$ is the average number, per lattice site, of the clusters, and a_{sm} the total number of geometrically different configurations for a cluster of s sites and perimeter m . Thus, $A_s(p) = \sum_m a_{sm} p^s (1-p)^m$. Enumeration of lattice animals is a difficult problem (Aleksandrowicz and Barequet 2011). The asymptotic behavior of $A_s(p)$ for large values of s is described by the power law

$$A_s(p) \sim s^{-\theta}, \quad (10)$$

where θ is a universal exponent, independent of the coordination number of the lattice. Moreover, for large values of s a fractal dimension D_f , defined by

$$s \sim R^{D_f}, \quad (11)$$

describes the structure of the animals or the branched polymers, where R is the radius of the lattice animal. Note that the fractal dimension D_f is *distinct* from that of critical gels given by Eq. (9). Lubensky and Isaacson (1978) and Family and Coniglio (1980) showed that the exponents θ and D_f are not related to any of the percolation exponents defined earlier. Moreover, Parisi and Sourlas (1981) derived the following scaling relation:

$$\theta = \frac{d-2}{D_f} + 1, \quad (12)$$

and that

$$D_f = 2, \quad d = 3. \quad (13)$$

Recall that the percolation exponents are defined for $p \simeq p_c$, whereas one key difference between lattice animals and percolation clusters is that the exponents θ and D_f are defined for *any* $p < p_c$, so long as R , the animals' radius, is much larger than the correlation length ξ . For this reason, the exponents associated with lattice animals are called *non-critical* exponents.

One may also define a pair correlation function $C(r)$, that is, the probability that two monomers (or sites) that are separated by a distance r , belong to the same polymer (cluster). For a d -dimensional branched polymer and large r , we expect the correlation function to decay as

$$C(r) \sim r^{D_f-d}. \quad (14)$$

The Fourier transform of $C(r)$ is proportional to the scattered intensity $I(q)$ in an X-ray or a neutron scattering experiment, where q is the magnitude of the scattering vector, $q = (4\pi/\zeta) \sin(\theta_s/2)$, with ζ being the wavelength of the radiation scattered by the material through the angle θ_s . Thus, by Fourier transforming Eq. (14), one obtains

$$I(q) \sim q^{-D_f}. \quad (15)$$

In practice, however, polymer solutions are almost always polydispersed and contain polymers of all sizes with radii that may be smaller or larger than the correlation length ξ . Thus, one must define *average* properties, with the averaging taken over the polymer size distribution. An average polymer radius is defined by,

$$\langle R \rangle = \frac{\sum_s s^2 R(s) Q(s, \epsilon)}{\sum_s s^2 Q(s, \epsilon)}, \quad (16)$$

which, when combined with Eqs. (3) and (11), yields a relation between s and $\langle R \rangle$ (Daoud et al. 1984):

$$s \sim \langle R \rangle^{D_f(3-\tau)}, \quad (17)$$

so that, in analogy with Eq. (11), an *effective fractal dimension*, $D_f^e = D_f(3-\tau)$, may be defined. Note that, Eq. (17) mixes the branched polymers' fractal dimension D_f with the gel exponent τ . If a percolation description of polymerization is correct, which the experiments described earlier confirmed it to be the case, we should have,

$$D_f^e \simeq 1.64, \quad d = 3, \quad (18)$$

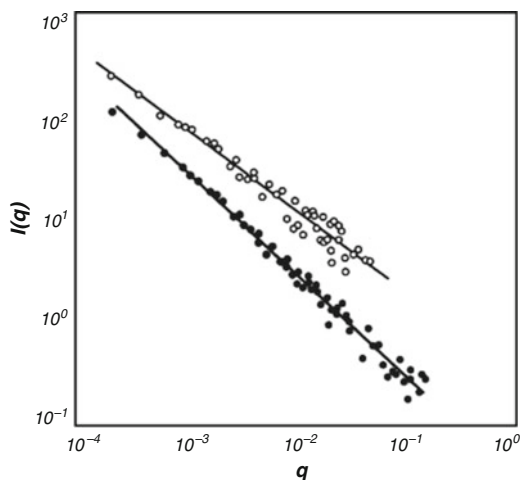
indicating that the effective fractal dimension is smaller than that of a single branched polymer. Because an effective fractal dimension has been defined for a dilute polydisperse polymer solution, the scattering intensity for the same solution should also be modified to

$$I(q) \sim q^{-D_f(3-\tau)}. \quad (19)$$

Comparison of the Experimental Data with the Predictions of the Lattice Animal Model

Experimental evidence for Eq. (13) is actually provided through Eqs. (15) and (19). Bouchaud et al. (1986) carried out small-angle neutron scattering experiments on a monodisperse polyurethane sample and measured the scattered intensity as a function of q . Figure 3 presents their data from which one obtains $D_f = 1.98 \pm 0.03$, in excellent agreement with Eq. (19). Bouchaud et al. (1986) also synthesized a natural polydisperse polyurethane sample and carried out small-angle neutron scattering on a dilute solution of it. Their data yielded the estimate, $D_f^e \simeq 1.6 \pm 0.05$, in good agreement with the theoretical prediction given by Eq. (18).

Adam et al. (1987) carried out static light scattering experiments with dilute polydisperse polyurethane solutions and reported that $D_f^e \simeq 1.62 \pm 0.08$, in good agreement with Eq. (18). Leibler and Schosseler (1985) measured the average radius of polystyrene, cross-linked by irradiation by elastic light scattering and found that $D_f^e \simeq 1.75 \pm 0.09$, relatively close to the estimate



Percolation and Polymer Morphology and Rheology, Fig. 3 Small-angle neutron scattering data for branched polymers. The upper curve is for a polydisperse polymer solution with a slope -1.6 . The lower curve is for a single polymer in a good dilute solvent with a slope -1.98 . (After Bouchaud et al. 1986)

provided by Eq. (18). Patton et al. (1989) carried out both quasi-elastic and elastic light scattering experiments on branched polyesters and reported that $D_f^e \simeq 1.52 \pm 0.1$, somewhat lower than the prediction (Eq. 18), but still consistent with it.

Rheology of Critical Gels

Rheological measurements provide clear understanding on what happens to the polymers as the GP is approached. Such experiments were described in detail by Winter and Mours (1997) and, therefore, we provide only brief description of them and discuss their implications. In such experiments one imposes a small step shear strain ϵ_{zx} on a sample near the GP and measures the shear stress $\sigma_{zx}(t)$ as a function of time t . The key property is then the shear stress relaxation function, $G(t) = \sigma_{zx}/\epsilon_{zx}$, which is also referred to as the *relaxation modulus*. Unlike the elastic moduli, $G(t)$ can be measured for both liquids and solids and, therefore, it is a very useful property for studying the sol-gel transition and, more generally, any LST. Note that t , the time of crosslinking reaction, corresponds to the extent p of the reaction, the key parameter in percolation theory.

How does $G(t)$ evolve as the GP is approached? The stress relaxes quickly at the early stages of cross-linking. As more chemical bonds are formed between the monomers, however, $G(t)$ stretches out further, since the relaxation process requires longer times. Exactly at the GP and, more generally, at any LST point, the material is neither a liquid nor a solid yet, because it has a tenuous fractal structure. The relaxation modulus follows a power law:

$$G(t) = G_0 t^{-n}, \quad t_0 < t < \infty \quad (20)$$

where G_0 is the gel stiffness. The parameters G_0 , n , and t_0 all depend on the material's structure at the GP. The exponent n is closely related to those that characterize the power-law behavior of the viscosity of sol and the elastic moduli of the gel network near the GP; see below. As the polymerization proceeds further and the GP p_c is passed, the material becomes a solid with a finite relaxation modulus at long times, usually referred to as the equilibrium modulus G_e :

$$G_e = \lim_{t \rightarrow \infty} G(t). \quad (21)$$

Under such conditions, the stresses can no longer relax completely.

The Spectrum of the Relaxation Times

Since the time-dependence of a macroscopic relaxation process is always indicative of the underlying microscopic dynamics, one may look for kinetic equations that correctly describe the time-dependence of the measured responses of a material. In the simplest case, there is only a single characteristic time τ , the origin of which goes back to Debye who proposed it in his seminal work on the dielectric response of polar liquids in 1913. If we define a shear compliance $J(t)$ – the inverse of the shear modulus – by

$$J(t) = \frac{\epsilon_{zx}}{\sigma_{zx}^0},$$

then applying an oscillatory shear stress

$$\sigma_{zx}(t) = \sigma_{zx}^0 \exp(i\omega t),$$

to a polymer means imposing an oscillatory strain, $\epsilon_{zx}(t) = \Delta J \sigma_{zx}(t)$. Here, ΔJ is the *relaxation strength* of the material. The governing equation for $\epsilon_{zx}(t)$ is then given by

$$\frac{d\epsilon_{zx}(t)}{dt} = -\frac{1}{\tau} [\epsilon_{zx}(t) - \Delta J \sigma_{zx}^0 \exp(i\omega t)]. \quad (22)$$

Assuming a solution, $\epsilon_{zx}(t) = \sigma_{zx}^0 J^*(\omega) \exp(i\omega t)$, where $J^*(\omega)$ is the *complex shear compliance*, substituting it into Eq. (22) and solving it yield

$$J^*(\omega) = \frac{\Delta J}{1 + i\omega\tau}, \quad (23)$$

which is usually referred to as a *Debye process*.

As discussed earlier, however, the dynamics of polymers and gels in the reaction bath cannot be described by a single relaxation time, rather by a statistical distribution of such characteristics times. For example, for the shear properties we write the dynamic compliance $J^*(\omega)$ as a sum of the Debye processes with relaxation times τ_i and relaxation strengths ΔJ_i , so that

$$J^*(\omega) = J_u + \sum_i \frac{\Delta J_i}{1 + i\omega\tau_i}. \quad (24)$$

The sum is usually replaced by an integral, so that

$$J^*(\omega) = J_u + \int \frac{\mathcal{R}(\tau)}{1 + i\omega\tau} d\tau, \quad (25)$$

where $\mathcal{R}(\tau)$ is called the *retardation time spectrum* of the shear compliance J^* . One may also write these results in terms of the complex modulus $G_{\text{eff}}^*(\omega) = 1/J^*(\omega)$, which then yields

$$G^*(\omega) = G_u - \int \frac{H(\tau)}{1 + i\omega\tau} d\tau, \quad (26)$$

where $H(t)$ is the *relaxation time spectrum* of the complex modulus $G^*(\omega)$ [or $G(t)$]. In practice, $H(t)$ cannot be directly measured, but is inferred only indirectly.

Dynamic Mechanical Experiments

The evolution of the molecular structure of a polymer during the gelation process has a profound effect on the molecular mobility, which can be monitored by probing the changes in the viscosity and elastic moduli. The initial ($p = 0$) liquid system has a steady shear viscosity η that increases with the extent of the reaction as the average molecular weight M_w increases. At the GP, the viscosity and the longest relaxation time τ_{max} diverge. Beyond p_c , the equilibrium elastic moduli increase until they attain their highest values, which is when the reaction is brought to completion, that is, when $p \rightarrow 1$.

All the experimental data for the elastic moduli of the nearly critical gel network indicate that the effective elastic moduli G_{eff} follow a power law:

$$G_{\text{eff}} \sim (p - p_c)^z, \quad p > p_c. \quad (27)$$

On the other hand, near the GP, the viscosity of the sol phase also follows a power law, resulting in its divergence at the GP:

$$\eta \sim (p_c - p)^{-k}, \quad p < p_c, \quad (28)$$

while, as shown below, the longest relaxation time diverges as

$$\tau_{\text{max}} \sim |p - p_c|^{-k-z}, \quad |p - p_c| \ll 1. \quad (29)$$

The divergence of the viscosity at the GP is precisely due to the divergence of the mean polymer (cluster) size at the GP that, near the GP, follows a power law similar to Eq. (6) for the weight-average molecular weight M_w with precisely the same exponent γ .

In practice, it is precisely the divergence of η that signals the formation of the critical gel network. Due to the divergence of τ_{max} , measurements of the viscosity and elastic moduli fail at p_c , since steady-state conditions cannot be reached in a finite time. Another difficulty is that precise measurement of the GP is often difficult. Such difficulties are partially overcome by performing *dynamic mechanical experiments*. In such experiments the sample is exposed to a

periodically varying stress held. For example, a tensile stress $\sigma_{zz}(t)$,

$$\sigma_{zz}(t) = \epsilon_{zz}^0 \exp(i\omega t), \quad (30)$$

is used that results in a time-dependent longitudinal strain $\epsilon_{zz}(t)$ that varies with the frequency of the stress, but exhibits, in general, a phase-lag φ such that

$$\epsilon_{zz}(t) = \epsilon_{zz}^0 \exp[-i(\omega t - \varphi)]. \quad (31)$$

We may then employ a *dynamic tensile modulus* $G^*(\omega)$, defined as

$$G^*(\omega) = \frac{\sigma_{zz}(t)}{\epsilon_{zz}(t)} = G'(\omega) + iG''(\omega). \quad (32)$$

Analogous experiments can, of course, be carried out for other types of mechanical loading. Of particular interest are measurements under simple shear that determine the relation between the shear strain ϵ_{zx} , yielding the displacement along x per unit distance normal to the shear plane $z = \text{constant}$, and the shear stress σ_{zx} that acts on the shear plane along x .

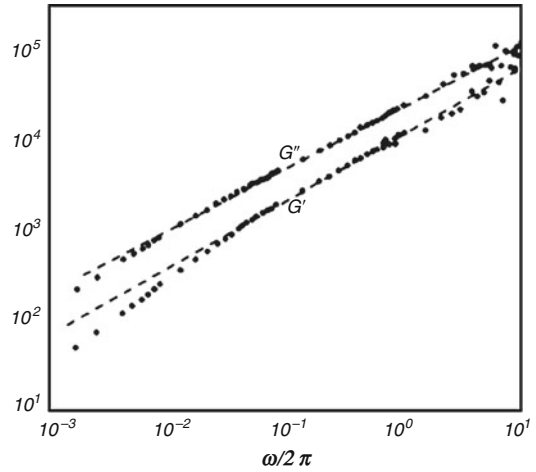
In any case, such dynamic mechanical experiments measure the small amplitude oscillatory shear behavior of evolving gels. Under such conditions, the gel evolution is continuous, exhibiting no singularity. But, even such experiments cannot entirely overcome the difficulties in the determination of the exponent k of the viscosity, because the measurements cannot be carried out *at* the GP and in the limit of *zero frequency*. To estimate k one usually measures the frequency-dependent complex modulus $G^*(\omega)$ at frequency ω . At the GP and for low frequencies, one has

$$G' \propto G'' \sim \omega^n, \quad p = p_c, \quad (33)$$

with

$$n = \frac{z}{z+k}, \quad (34)$$

where G' , the storage modulus, and G'' , the loss modulus, describe storage and dissipation in an oscillating strain field of constant amplitude. Note



Percolation and Polymer Morphology and Rheology, Fig. 4 Frequency-dependence of the storage modulus G' and loss modulus G'' for a polycondensed gel close to the gel point. (After Durand et al. 1987)

that the exponent n in Eq. (34) is the same as that in Eq. (20). Typical variations of G' and G'' with ω are shown in Fig. 4 for a polycondensed gel very close to the GP.

The complex modulus $G^*(\omega)$ is sometimes written as $G^* = G + i\omega\eta$, for which Durand et al. (1987) proposed that

$$G^*(\omega, \epsilon) \sim \epsilon^z h_3\left(i\omega|p - p_c|^{z+k}\right), \quad (35)$$

where $h_3(x)$ is a universal scaling function. The significance of scaling equation (35) is that it enables one to collapse the data for all values of $|p - p_c|$ and ω onto a single curve, usually called the *master curve* by polymer researchers. In the low-frequency regime, we do not expect $G^*(\omega)$ to depend on $|p - p_c|$, but only on ω , in which case one finds that $G^* \sim (i\omega)^n$, which is equivalent to Eq. (33). Moreover, there is a loss angle δ defined by $\tan\delta = G'/G''$. The remarkable property of δ is that at the GP it takes on a value δ_c given by

$$\delta_c = \frac{\pi}{2}(1 - n) = \frac{\pi}{2} \frac{k}{z+k}. \quad (36)$$

so that, if the exponents z and k are universal, so will also be the loss angle δ_c .

The Spectrum of Self-Similar Relaxation Times

The observed power-law behavior of G' and G'' , Eq. (33), implies the existence of a relaxation time spectrum, which is self-similar in time:

$$H(t) = \frac{G_0}{\Gamma(n)} \left(\frac{t}{\tau_0} \right)^{-n}, \quad (37)$$

where G_0 is a characteristic modulus, τ_0 is the characteristic *shortest relaxation time*, and Γ is the gamma function. The modulus of a fully cross-linked polymer network is typically 10^6 – 10^7 Pa, while the relaxation time of the network strand is about 10^{-7} – 10^{-4} s. The spectrum $H(t)$ extends from the shortest time, at which the strands are beginning to be probed, to the infinite relaxation time of the critical gel network. The parameters G_0 and τ_0 are material characteristics of the gel system. Most gels seem to possess the same value of n . However, there are also gels that exhibit no apparent universality in the value of n .

Viscosity and elastic moduli are rheological and mechanical properties of branched polymers and gels that characterize the dynamics of polymerization, since we may measure indirectly the distribution of the relaxation times $H(t)$ in the reaction bath. The moments of $H(t)$ are directly related to the viscosity and the elastic moduli. Using Eqs. (35) and (37), we back-calculate $H(t)$ (Family and Coniglio 1980):

$$H(t) \sim t^{-n} h_4 \left(t |p - p_c|^{z+k} \right), \quad (38)$$

where h_4 is another universal scaling function. Equation (38), which indicates that in the scaling regime near the GP the relaxation time distribution is a slowly decaying power law, generalizes Eq. (37) to any value of p , the extent of the polymerization. Equations (37) and (38) indicate that *any* relaxation property in the intermediate time or frequency range is *not* exponential, but follows a power law. As pointed out by Daoud (1988), two distinct averages or characteristic times may be defined. One is

$$\tau_1 = \frac{\int H(t) dt}{\int [H(t)/t] dt} \sim |p - p_c|^{-k} \propto \eta, \quad (39)$$

whereas the second one is given by

$$\tau_2 = \frac{\int t H(t) dt}{\int H(t) dt} \sim |p - p_c|^{-z-k}. \quad (40)$$

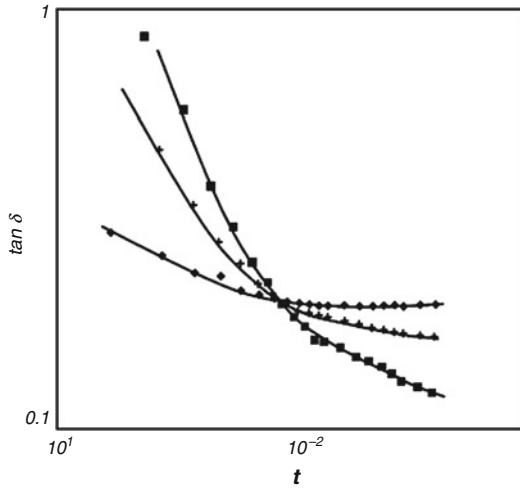
Note that τ_2 is, in fact, identical with $\tau_{\max}$, the longest relaxation time of gels; see Eq. (29).

Determination of the Gel Point

As mentioned earlier, an important problem in polymerization and gelation is accurate determination of the GP, either for avoiding it in order to prevent gelation, so that a branched polymer with specific properties can be prepared, or for making polymeric materials very close to the GP, as they have unusual properties near the GP. The GP, which is the analogue of a percolation threshold, depends on the functionality Z of the polymer – the analogue of the coordination number in the lattice models – and decreases with increasing Z . Thus, polymers with cross-links of high functionality gel very early. The Winter group (Holly et al. 1988; Lin et al. 1991) proposed using the loss angle δ for locating the GP. They reasoned that because as the GP is reached $\tan \delta$ becomes independent of the frequency (see Eq. 36), then, if one plots $\tan \delta$ versus time at various frequencies, the intersection of all the curves should be at the GP. Figure 5 demonstrates how this method is used for locating the GP for a physical gel.

Resistor and Elastic Percolation Networks

Experimental data for the scaling properties of the elasticity and viscosity of gels are usually compared with those of the conductivity and elasticity of percolation networks. Thus, we first briefly summarize percolation models of the conductivity of a percolation network. Consider a two-component network in which each randomly selected bond has a conductance g_1 with probability p , or a conductance g_2 with probability



Percolation and Polymer Morphology and Rheology, Fig. 5 Determination of gel point from data for loss angle δ . Time is in minutes. The data are for frequencies 31.6 rad/s (diamonds), 1.0 rad/s (+), and 0.0316 rad/s (squares). (After Lin et al. 1991)

$1 - p$. The limit in which $g_2 = 0$ and g_1 is finite corresponds to a conductor-insulator mixture. As $p \rightarrow p_c$, more and more bonds are insulating. Thus, the conduction paths become very tortuous and, therefore, the effective conductivity g_{eff} of the network decreases. At p_c one has, $g_{\text{eff}}(p_c) = 0$, since no sample-spanning conduction path exists any more. In the critical region near p_c the effective conductivity follows a power laws:

$$g_{\text{eff}}(p) \sim (p - p_c)^t \quad \begin{array}{l} \text{conductor} \\ \text{-- insulator networks.} \end{array} \quad (41)$$

The limit in which $g_1 = \infty$ and g_2 is finite represents a *conductor-superconductor* mixture. All quantum-mechanical aspects of real superconductors are ignored in this definition, as we are concerned only with the effect of the local connectivity of the material on g_{eff} . It should be clear that the effective conductivity g_{eff} of the network is dominated by the superconducting bonds. If $p < p_c$, then a sample-spanning cluster of the superconducting bonds does not exist, and (σ_{eff} is finite). As $p \rightarrow p_c^-$, however, g_{eff} increases until a sample-spanning cluster of the superconducting bonds is formed for the first time at $p = p_c$, where

g_{eff} *diverges*. In the region $p \rightarrow p_c^-$, the effective conductivity follows a power law:

$$g_{\text{eff}}(p) \sim (p_c - p)^{-s} \quad \begin{array}{l} \text{conductor} \\ \text{-- superconductor networks.} \end{array} \quad (42)$$

The exponents t and s are mostly universal. The chapter ► “Principles of the Theory of Continuum Percolation” by Balberg describes the conditions under which they may be non-universal.

In a similar manner, the elastic moduli of a two-phase percolation network are defined. Consider a two-component network in which each bond is an elastic element – a spring or a beam – with an elastic constant e_1 with probability p , or e_2 with probability $1 - p$. The limit in which $e_2 = 0$ and e_1 is finite corresponds to a mixture made of rigid materials and holes, such as, for example, a porous solid, or a mixture of rigid and liquid materials. In such networks, as $p \rightarrow p_c$, an increasingly larger fraction of the bonds have no rigidity. Thus, the paths for transmission of stress or elastic forces become very tortuous and, therefore, the effective elastic moduli G_{eff} – the Young’s, bulk, or shear moduli – decrease. We refer to this model as an elastic percolation network. At p_c one has $G_{\text{eff}}(p_c) = 0$, while near p_c in the critical region,

$$G_{\text{eff}}(p) \sim (p - p_c)^T \quad \begin{array}{l} \text{rigid} \\ \text{-- soft elastic networks.} \end{array} \quad (43)$$

The limit in which $e_1 = \infty$ and e_2 is finite represents a mixture of rigid-superrigid materials. We refer to the model as the *superelastic percolation network*. In this case the effective elastic moduli G_{eff} of the network are dominated by the superrigid bonds. If $p < p_c$, then a sample-spanning cluster of the superrigid bonds cannot form, and G_{eff} is finite. As $p \rightarrow p_c^-$, however, the effective elastic moduli increase until the percolation threshold p_c of the rigid phase is reached at which a sample-spanning cluster of the superrigid bonds is formed for the first time, and the effective elastic moduli *diverge*. In the critical region near p_c one has

$$G_{\text{eff}}(p) \sim (p_c - p)^{-S} \quad \text{rigid} \\ - \text{superrigid networks.} \quad (44)$$

Unlike the exponents t and s for resistors networks, the exponents T and S may depend on the details and the type of the forces that are active in the networks. Thus, in what follows, we first briefly describe various types of forces that have been considered in such elastic networks.

The Born Model

The Born model (Born and Huang 1954) is described by the following elastic Hamiltonian:

$$\mathcal{H} = \frac{1 + \mathcal{P}}{1 - \mathcal{P}} \sum_{ij} \mu [(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{R}_{ij}]^2 \\ + \frac{1 - 3\mathcal{P}}{4(1 - \mathcal{P})} \sum_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2, \quad (45)$$

where $\mathcal{P}$ is the Poisson's ratio, μ the shear modulus, $\mathbf{u}_i$ the displacement of site i , and $\mathbf{R}_{ij}$ the unit vector along the line (lattice bond) that connects sites i and j . The first term of Eq. (45) is the energy of a network of central-force (CF) springs, that is, Hookean springs that transmit force only in the $\mathbf{R}_{ij}$ direction, but do not transmit shear forces. The second term is a contribution analogous to, for example, the power dissipated in conduction, since $(\mathbf{u}_i - \mathbf{u}_j)^2$ represents the *magnitude* of the displacement difference $\mathbf{u}_i - \mathbf{u}_j$, similar to a voltage difference. The Born model may be considered as an analogue of a 3D solid in plane-stress with holes normal to the x - y plane, or as a 2D solid with the Poisson's ratio defined as the negative of ratio of the strain in the y -direction to that in the x -direction, when a stress is applied in the x -direction, but none is applied in the y -direction. Results for a 3D solid in plane-strain can be generated from those of this model using the transformation, $\mathcal{P}' = \mathcal{P}/(1 + \mathcal{P})$, where $\mathcal{P}'$ is the Poisson's ratio for the plain strain.

The Born model does suffer from some peculiarities. For example, it is not difficult to show (although it may not be obvious at first glance)

that, except for $\mathcal{P} = 1/3$, the elastic energy $\mathcal{H}$ defined by Eq. (45) is *not* invariant with respect to arbitrary rigid body rotations, a fundamental requirement for any reasonable model of elastic properties of materials. In the limit $\mathcal{P} = 1/3$ the model reduces to a network of CF springs. When the elastic energy of a system is written in terms of an expansion in the displacement held $\mathbf{u}$, its rotational invariance is not easy to see. To demonstrate the lack of rotational invariance of the elastic energy, one substitutes an infinitesimal rotation $\boldsymbol{\omega} \times \mathbf{R}_i$ for the displacement vector $\mathbf{u}_i$, where $\mathbf{R}_i$ is the position vector of i . An arbitrary rotation of the solid should not contribute to its energy, but Eq. (45) indicates that, while the contribution of the CF part would indeed be zero, that of the scalar-like part would not be and, therefore, $\mathcal{H}$ is not rotationally invariant. Moreover, although materials do exist that have a Poisson's ratio as high as $1/2$ ($\mathcal{P}$ can theoretically be as high as 1 in 2D materials (Sahimi, 2003)), the model fails to have a strictly positive energy for $\mathcal{P} > 1/3$ and, therefore, violates the thermodynamic requirement that the potential energy must be a minimum at zero strain. Another example of displacements that contribute to the scalar-like portion of the energy $\mathcal{H}$ of the model, but not to the CF portion, arises when a significant fraction of the lattice's bonds is removed, that is, an elastic percolation network is generated. In such a lattice a site connected to only one bond can have an arbitrary displacement in the direction orthogonal to the direction of the bond without affecting the CF part of the elastic energy, as can a site connected to only a set of two collinear bonds.

In his original formulation of the model, Born (Born and Huang 1954) inserted the scalar-like part of the elastic energy (Eq. 45) as a substitute for the many-body, angular and bending terms (see below) that normally arise in describing the elastic properties of materials, because the expansion of such scalar two-body terms is much simpler and more convenient than expanding the many-body terms that they replace. When viewed in this way, the coefficients of the model should be treated as fitting parameters. Hence, let us rewrite Eq. (45) as

$$\mathcal{H} = \frac{1}{2} \alpha_1 \sum_{ij} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{R}_{ij}]^2 + \frac{1}{2} \alpha_2 \sum_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2, \quad (46)$$

where α_1 and α_2 now represent two adjustable parameters. One may then use the Born model for modeling and fitting elastic properties of certain materials.

Note that, so long as $\alpha_2 > 0$, the scalar-like term of Eqs. (45) or (46) is the dominant contributing factor to the elastic energy $\mathcal{H}$. This implies immediately that, although the Born model is a vector model, the behavior of the elastic moduli in this model near the percolation threshold is effectively like that of a scalar (conductivity) model and, therefore,

- (i) the percolation threshold of the Born model, at which the elastic moduli vanish or diverge, is the same as that of random percolation models, and
- (ii) near the percolation threshold the elastic moduli of the Born model follow power law (43) or (44), but with $T = t$ and $S = s$. That is, the power-law behavior of the elastic moduli in the Born model is the same as that of the effective conductivity.

The Central-Force Model

Consider the limit $\mathcal{P} = 1/3$ of Eq. (45), that is, a network of CF or Hookean springs. Since the elastic materials that we wish to consider are heterogeneous, the local shear modulus μ varies spatially. Thus, writing $\mu = e_{ij}\alpha/4$ and taking $\mathcal{P} = 1/3$ reduce Eq. (45) to

$$\mathcal{H} = \frac{1}{2} \alpha \sum_{ij} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{R}_{ij}]^2 e_{ij} \quad (47)$$

where α is the CF constant.

The elastic moduli of the CF networks can be computed straightforwardly, if no percolation effect is present, that is, if no bond is broken and

all the e_{ij} are equal. Suppose that each spring has an unstretched length ℓ_0 . Then, it is not difficult to show that the bulk modulus K of a triangular network is given by (Sahimi 2003)

$$K = \frac{\sqrt{3}}{2} \alpha \quad \text{triangular network}, \quad (48)$$

whereas its shear modulus is given by (Sahimi 2003)

$$\mu = \frac{\sqrt{3}}{4} \alpha \quad \text{triangular network}, \quad (49)$$

and, therefore, the Poisson's ratio of the network is, $\mathcal{P} = (K_e - \mu_e)/(K_e + \mu_e) = 1/3$. Similarly, we may show that (Sahimi 2003),

$$K = \mu_p = \frac{1}{2} \alpha \quad \text{square network}, \quad (50)$$

where μ_p is the shear modulus in *pure* shear (the network's shear modulus in *simple* shear is zero). As for the standard 3D cubic networks, one has (Sahimi 2003)

$$K_e = \begin{cases} \frac{1}{3\ell_0} \alpha & \text{simple - cubic network,} \\ \frac{1}{\sqrt{3}\ell_0} \alpha & \text{BCC network,} \\ \frac{2\sqrt{2}}{\sqrt{3}\ell_0} \alpha & \text{FCC network.} \end{cases} \quad (51)$$

A simple-cubic network does not possess a shear modulus in simple shear. We emphasize that Eqs. (48), (49), (50), and (51) are valid at zero temperature and when the external stress is infinitesimally small.

In practice, however, all the experimental measurements are carried out at temperatures above $T = 0$ and, therefore, it is important to understand the temperature-dependence of the elastic moduli, at least in the context of the network models. In addition, in many practical situations, the material under study is exposed to a finite stress or tension (as opposed to an infinitesimal stress or tension considered above) and, thus, the role of such an

external driving force in determining the elastic properties of materials must be understood. In principle, the role of the temperature can be understood by carrying out molecular dynamics simulations (Plischke and Joós 1998). However, phenomenological calculations of the type described above can also be carried out for homogeneous networks at non-zero temperature. Suppose, then, that a 2D isotropic tension σ_i is imposed on a network at a non-zero temperature. One can show that for the triangular network (Sahimi 2003)

$$K = \frac{1}{2}(\sqrt{3}\alpha - \sigma_i), \quad (52)$$

$$\mu = \frac{\sqrt{3}}{4}(\alpha + \sqrt{3}\sigma_i), \quad (53)$$

which reduce to Eqs. (48) and (49) in the limit $\sigma_i = 0$. Similar results are obtained for the square network (Sahimi 2003):

$$K = \frac{1}{2}(\alpha - \sigma_i), \quad (54)$$

$$\mu_p = \frac{1}{2}(\alpha + \sigma_i), \quad (55)$$

$$\mu_s = \sigma_i, \quad (56)$$

where μ_s is the shear modulus of the network in simple shear.

Rigidity Percolation

If the elastic constants e_{ij} of the bonds of a CF network take on either a finite value with probability p or vanish with probability $1 - p$, then one obtains an elastic percolation network with central forces. If e_{ij} is infinitely large with probability p , or takes on a finite value with probability $1 - p$, then one obtains a superelastic percolation network with central forces. Percolation on such networks of Hookean springs is called the *rigidity percolation*. Such networks are of both theoretical and practical interest. In addition to the polymeric materials described in this chapter, they are also useful models for describing the elastic properties of biological materials. Moreover, in many engineering problems, structures composed of bars or

beams connected at nodes that are called trusses acquire their rigidity mainly from the tensile and compressive stiffness of the beams, which are CF type of contributions. For example, in the absence of friction between the particles of a granular packing, which is a reasonable model of unconsolidated porous materials such as powders, the mechanical behavior of the packing is similar to those of rigidity percolation. In contrast, those in which angular forces, for example, covalent bonds at the molecular level, are the most important are usually referred to as *frames*. It is not difficult to see that rigid systems in which angular forces dominate their behavior support an applied stress, so long as they are simply connected. In contrast, the CF systems require higher degrees of connectivity. Therefore, the percolation thresholds of CF networks are much larger than those of random percolation networks; see the chapters ▶ “Elastic Percolation Networks” and ▶ “Networks, Flexibility and Mobility in” by Duxbury and Thorpe.

The Bond-Bending Model

Consider an elastic percolation network in which there are both central and bond-bending (angle-changing) forces, with the latter type representing the three-body interactions. One of the main advantages of such a model is that their percolation threshold can be the same as that of random percolation, if the many-body interactions are such that any deformation of the lattice is done at some cost to its elastic energy. In general, the elastic energy of such models is given by (Kantor and Webman 1984)

$$\mathcal{H} = \frac{1}{2}\alpha \sum_{\langle ij \rangle} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{R}_{ij}]^2 e_{ij} + \frac{1}{2}\chi \sum_{\langle jik \rangle} (\delta\theta_{jik})^2 e_{ij}e_{ik}, \quad (57)$$

where α and χ are, respectively, the central and bond-bending (BB) force constants. Here, $\langle jik \rangle$ indicates that the sum is over all triplets in which the bonds $j-i$ and $i-k$ form an angle with its vertex at i . The first term on the right-hand side of Eq. (57) represents the usual CF contributions

(see above), while the second term is due to the BB (angle-changing) forces. The precise form of $\delta\theta_{jik}$ depends on the microscopic details of the

model. In the version that is of interest to us, bending of the collinear bonds is allowed, in which case (Wang 1989; Arbabi and Sahimi 1990a)

$$\delta\theta_{jik} = \begin{cases} (\mathbf{u}_{ij} \times \mathbf{R}_{ij} - \mathbf{u}_{ik} \times \mathbf{R}_{ik}) \cdot (\mathbf{R}_{ij} \times \mathbf{R}_{ik}) / |\mathbf{R}_{ij} \times \mathbf{R}_{ik}|, & \mathbf{R}_{ij} \text{ not parallel to } \mathbf{R}_{ik}, \\ |(\mathbf{u}_{ij} + \mathbf{u}_{ik}) \times \mathbf{R}_{ij}|, & \mathbf{R}_{ij} \text{ parallel to } \mathbf{R}_{ik}, \end{cases} \quad (58)$$

where $\mathbf{u}_{ij} = \mathbf{u}_i - \mathbf{u}_j$. For *all* 2D networks, Eq. (58) is simplified to

$$\delta\theta_{jik} = (\mathbf{u}_i - \mathbf{u}_j) \times \mathbf{R}_{ij} - (\mathbf{u}_i - \mathbf{u}_k) \times \mathbf{R}_{ik}. \quad (59)$$

We refer to the model described by Eqs. (57), (58), and (59) as the BB model. For most materials to which the BB model is applicable, one has $\chi/\alpha \leq 0.3$ (Martins and Zunger 1984). Sahimi (1986) suggested that the critical exponent T of the elasticity in the BB model is related to t , the critical exponent of conductivity of percolation networks:

$$T = t + 2\nu, \quad (60)$$

where ν is the correlation length exponent of percolation. This relation is in excellent agreement with the available numerical estimates (see Table 1). The chapters ► “Elastic Percolation Networks” and ► “Networks, Flexibility and Mobility in” by Duxbury and Thorpe provide much more detailed discussions of the CF and BB models and, therefore, we do not discuss them any further.

Before embarking on a comparison between the experimental data for the rheological properties of near critical gels, for convenience and as a basis for comparison with the experimental data, we summarize in Table 1 the current most accurate estimates of the various critical exponents for the conductivity and elasticity of percolation models near the percolation thresholds, including the CF and BB models.

We are now in a position to compare the predictions of the percolation models with the experimental data for the viscosity of the nearly critical sol, and the elastic moduli of the nearly critical gels.

Nearly Critical Chemical Gels: Comparison of Experimental Data with the Percolation Models

There are numerous experimental measurements of the elastic moduli of nearly critical chemical gels and the associated exponent z . Examples include the measurements for hydrolyzed polyacrylamide (Allain and Salomé 1987a, 1990), tetraethylorthosilicate reactions (Hodgson and Amis 1990; Takahashi et al. 1994), gelatin solutions (Djabourov et al. 1988), polycondensation

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Table 1 Estimates of the critical exponents of the conductivity and elastic moduli of percolation models in d -dimensions. Values of T and S for the CF model refer to bond percolation, whereas those of t and s , the conductivity

exponents, are independent of the model, ν is the critical exponent of the percolation correlation length. Value of ν for the CF model is different from that of random percolation, whereas for the BB model it is the same as that of random percolation

d	t/ν	s/ν	T/ν	S/ν	Model
2	0.9745 ± 0.0015	0.9745 ± 0.0015	2.97 ± 0.03	0.92 ± 0.03	Bond bending
	—	—	2.95 ± 0.25	0.92 ± 0.02	Central force
3	2.27 ± 0.01	0.835 ± 0.005	4.3 ± 0.1	0.74 ± 0.04	Bond bending
	—	—	2.1 ± 0.1	0.80 ± 0.03	Central force

of polyoxypropylated trimethylolpropane with hexamethylenediisocyanate (Durand et al. 1987), and several other sets of measurement (Gauthier-Manuel and Guyon 1980; Adam et al. 1981; Gordon and Torkington 1981; Tokita et al. 1984; Fadda et al. 2001). These measurements yielded estimates of z that are in the range of 1.9–2.4, which do not agree with the value of the critical exponent T for the 3D BB model shown in Table 1. In fact, if the size of a chemical gel network is large enough, the BB forces may not play any important role in determining the elastic properties of nearly critical gels and, therefore, the only important forces between the monomers are the central (stretching) forces. Therefore, these experimental data may be explained based on the elasticity exponent in the 3D CF percolation (Arbabi and Sahimi 1993), $T \simeq 2.1 \pm 0.2$.

However, a value of z in the range of 1.9–2.4 may also be interpreted in terms of two other models:

- (i) As mentioned earlier, de Gennes (1976) suggested that the scaling properties of the elastic moduli of nearly critical gels are in the universality class of the conductivity of percolation networks, implying that $z = t \simeq 2.0$.
- (ii) On the other hand, Alexander (1984) argued that there are contributions to the elastic energy of some gels and rubbers that are under internal or external stresses that are similar to the Born model. As discussed above, the critical exponent of the elastic moduli in the Born model is equal to that of the conductivity, t , and in particular in 3D, $T = t \simeq 2.0$, because near the percolation threshold the contribution of the second term of the right side of Eq. (45) or (46), which is a purely scalar term, dominates that of the first term which is due to the CFs.

While the data mentioned above are more or less consistent with de Gennes' hypothesis, most of them are not precise enough to distinguish between $t \simeq 2.0$ for 3D percolation conductivity and $T \simeq 2.1$ for the CF percolation. However, there are also a few relatively precise sets of experimental data that seem to support de Gennes' conjecture. For example, Axelos and Kolb (1990)

measured the rheological properties of pectin biopolymers that consist of randomly connected $\alpha(1-4)$ D-galacturonic acid units and their methyl esters. If the methyl ester content is low, pectin forms thermoreversible gels upon addition of cations, such as calcium. Axelos and Kolb (1990) measured the frequency dependence of the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ (see Eq. 33) and reported that $z \simeq 1.93$, $k \simeq 0.82$, and $n \simeq 0.71$. Their elasticity exponent is close to that of the conductivity, $t \simeq 2.0$, for 3D resistor networks. Less precise data, but still supportive of de Gennes' proposal, were reported by Adam et al. (1997) for the complex modulus of end-linked poly(dimethylsiloxane) pregel polymer clusters, quenched at different distances from the gelation threshold. They reported that $z \simeq 1.9 \pm 0.15$, consistent with the value of the conductivity exponent t for 3D percolation. However, the estimated error is large enough that one may also interpret such a value of z in terms of the CF percolation model.

At first glance, de Gennes' proposal that the critical exponent of the effective moduli of gels, a vector transport property, should be equal to that of a scalar property, the effective electrical conductivity of a resistor network, may seem incorrect. To justify his proposal, however, de Gennes introduced the notion of an elastic chain between neighboring nodes or monomers that are the analogue of quasi-one-dimensional strands that percolation clusters possess near the percolation threshold (see the chapter ► “Correlated Percolation” by Coniglio). He then argued that if such chains are elongated, their nodes would carry an extra amount of energy. If we assume that the blobs – the multiply-connected parts – of the large cluster of monomers do not contribute significantly to the elastic moduli, then one must only consider the energetics of the links or the chains. If the extra energy of such chains is larger than $k_B T$, with k_B being the Boltzmann's constant, then as Daoud (2000) argued, one obtains de Gennes' proposal (1976), $t = z$, although Daoud's analysis was a mean-held approximation, not a scaling one.

As for Alexander's proposal (1984), rubbers and gels differ from the Born model in several important ways, such as the presence of nonlinear terms in their elastic energy, and the possibility of negative as well as positive Born coefficients α_1

and α_2 in Eq. (46). Therefore, as discussed above, while one may use the Born model to *fit* the experimental data, it is not clear that, at a fundamental level, the Born model can actually describe the elastic properties of such gels, since its elastic energy is not rotationally invariant.

Enthalpic Versus Entropic Elasticity

There is yet another way of interpreting the experimental data for the scaling properties of nearly critical gels. Several sets of measurements of the elastic moduli of nearly critical gel and the associated exponent z deviate significantly from all the data described above. Examples include the measurements of Adam et al. (1985) for polycondensation, $z \simeq 3.3 \pm 0.5$, those of Martin et al. (1988) and Adolf et al. (1990) for gels made from 89% (by weight) of the diglycidyl ether of bisphenol A cured with 11% (by weight) of diethanolamine that yielded $z \simeq 3.3 \pm 0.3$, and the data reported by Colby et al. (1993) for polyester gels, which have been argued to lie in the middle of the static crossover between the Flory-Stockmayer (Bethe lattice) model, which predicts that $z = 3$, and the 3D percolation model. Colby et al. (1993) reported that $z \simeq 3.0 \pm 0.7$, which is inconsistent with both the CF percolation and the BB models, although one might argue that their estimate is agreement with $z = 3$, the Flory-Stockmayer prediction for z . More recent measurements of the shear modulus of an end-linking polymer gel network by Takahashi et al. (1994) yielded $z \simeq 2.7$, which is again in the range of the above data.

One possible explanation for such data is that the elasticity of such gels is entropic rather than enthalpic. Plischke and Joós (1998), Plischke et al. (1999), Farago and Kantor (2000), and Plischke (2006, 2007) proposed that the CF and the BB models are applicable to gels at temperature $T = 0$, and that for $T \neq 0$ there is an important contribution to the shear modulus that is entropic in nature. In analogy with the physics of rubber elasticity, Plischke et al. (1999) argued that, near the percolation threshold or the GP, the polymer network consists essentially of long chains of singly-connected monomers, linked to each other at various junction points. Such chains are similar to the polymer chains that are cross-linked in rubber in order to produce a rigid amorphous

material. Deformation of the sample changes the distance between the junction points or cross-links, as a result of which the entropy is generically decreased, resulting in an increase of free energy and, hence, a restoring force. There would be a net shear-restoring force, when the nearly critical gel is formed, implying that the connecting chain of particles acts as a stretched spring. Molecular dynamics simulations (for a review see, e.g., Kremer (1998)) of Plischke and coworkers and computer simulations of Farago and Kantor (2000), who used a model that consisted of hard spheres in which a fraction p of the neighbors were tethered by inextensible bonds, both yielded $z \simeq t$.

On the other hand, del Gado et al. (1999) proposed a different model, also purported to be appropriate for entropic gels, in which one begins with a random collection of monomers with concentration p . Each pair of the monomers are then linked with a probability p_b to form permanent bonds. Varying p_b produces a distribution of clusters of the bonded monomers and, hence, gives rise to the possibility of forming a sample-spanning cluster. The monomers and clusters then diffuse according to the bond fluctuation algorithm of Carmesin and Kremer (1988). In this algorithm, the monomers diffuse in the solution randomly, but satisfying the excluded-volume interaction that no two monomers can occupy the same point in space. Due to the random motion, the bonds may have to change their length in a set of allowed values and, thus, they may have to bend and take on many different values of the angles between the bonds, which then gives rise to a wide variety of polymer conformations. The mean-square displacement $\langle R^2(t) \rangle$ of the polymer's center of mass was then calculated that, due to the elastic potential that reduces the fluctuations proportional to the effective elastic constant α , is given by

$$\langle R^2(t) \rangle \propto \alpha^{-1}, \quad (61)$$

and, therefore, the elastic constant and its power-law behavior near the percolation threshold p_c can be computed, from which the exponent z is extracted. Two-dimensional simulations of del Gado et al. (1999) yielded the estimate, $z \simeq 2.7 \pm 0.1$,

hence disagreeing with the results of Plischke and coworkers and Farago and Kantor.

How can one interpret these results? If the elasticity of these gels is due to entropic effects, then, according to Daoud and Coniglio (1981) (see also Martin et al. (1988)), the elastic free energy $\mathcal{H}$ per unit volume must be given by

$$\mathcal{H} \sim \xi_p^{-d} \alpha_\ell \xi_p^2, \quad (62)$$

where ξ_p is the correlation length of percolation, and α_ℓ is the effective elastic constant of a long chain of length ξ_p connecting two nodes. Since $\alpha_\ell \sim \xi_p^{-2}$, we obtain

$$z = \nu d. \quad (63)$$

Since for 2D percolation, $\nu = 4/3$, Eq. (63) predicts that, $z = 8/3 \simeq 2.66$, quite different from the exponents T of both the CF and BB models, and also the conductivity exponent, $t \simeq 1.3$ (see Table 1), but in agreement with the numerical simulations of del Gado et al. (1999), Daoud (2000) argued that Eq. (63) is valid when the energy of the chains is of the same order of magnitude as the thermal energy $k_B T$.

Since, $\nu \simeq 0.89$ for 3D percolation, Eq. (63) predicts that, $z \simeq 2.67$, consistent with the experimental data of Adam et al. (1985), Martin et al. (1988), Adolf et al. (1990), Colby et al. (1993), and Takahashi et al. (1994) mentioned earlier, all of whom reported estimates of the elasticity exponent z in the range of $2.7\text{--}3.3 \pm 0.5$. Therefore, while these experimental data may be explained by Eq. (63), the numerical results of Plischke and coworkers (Plischke and Joós 1998; Plischke et al. 1999; Plischke 2006, 2007), as well as those of Farago and Kantor (2000), do not agree with the prediction of Eq. (63). Indeed, although the main argument of Plischke et al. (1999) was that the entropic effects are important at temperatures $T > 0$, where one should see a crossover to the conductivity exponent, all of the above experiments were also carried out at finite temperatures, yet they did not indicate that $z \simeq t$.

On the other hand, Xing et al. (2004) studied the scaling of shear modulus near the gelation-

vulcanization transition. They proposed that in a dense melt the sizes of the effective chains of the critical gel scale *sublinearly* with their contour length. The implication is that the energy that each chain contributes is of the order of $k_B T$, hence leading to Eq. (63). However, in *phantom* networks – those in which there is no repulsion between the particles (monomers) – the chains' sizes scale *linearly* with their contour length, which means that the elasticity exponent z crosses over to the conductivity exponent t . Thus, it may be that some of the conflicts between the various experimental estimates of z are due to the crossover effects, but the issue remains unsolved.

Viscosity of Nearly Critical Sol: Comparison of Experimental Data with the Percolation Models

There is also a wealth of experimental data for the viscosity of the nearly critical sol solution and the associated critical exponent k , defined by Eq. (28). An important question that has been studied for over two decades is: how can one explain the extensive experimental data for the scaling behavior of the viscosity η of the sol phase near the GP? To begin with, it was proposed by Sahimi and Goddard (1985) (see also Arbabi and Sahimi (1990b) and Sahimi and Arbabi (1993)) that the power-law behavior of η near the GP is analogous to that of the shear modulus of a superelastic percolation network near p_c and, therefore, the same critical exponent characterizes both. To proceed further, we must first establish a rigorous relationship between the linear elasticity and the theory of viscous fluids, thus confirming the proposal of Sahimi and Goddard (1985).

We consider a general time-dependent system for which the equation of motion for a macroscopically homogeneous material in terms of the displacement held $\mathbf{u}$ is given by:

$$(\lambda + \mu)\nabla(\nabla \cdot \mathbf{u}) + \mu\nabla^2 \mathbf{u} + \mathbf{F} = \rho \frac{\partial^2 \mathbf{u}}{\partial t^2}, \quad (64)$$

where ρ is the mass density, t the time, λ and μ the usual Lamé coefficients, and $\mathbf{F}$ an external force. For an *incompressible* material, that is, one for which the bulk modulus K and the Lamé

coefficient λ are both divergent, one has the solenoidal condition,

$$\nabla \cdot \mathbf{u} = 0. \quad (65)$$

Due to the incompressibility condition, the first term of Eq. (64) is indeterminate. Equation (64) can be then written in terms of the reactive hydrostatic pressure P ,

$$-\nabla P + \mu \nabla^2 \mathbf{u} + \mathbf{F} = \rho \frac{\partial^2 \mathbf{u}}{\partial t^2}. \quad (66)$$

On the other hand, let us consider the Navier-Stokes equations of motion for an incompressible and Newtonian viscous fluid,

$$-\nabla P + \eta \nabla^2 \mathbf{u} + \mathbf{F} = \rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right), \quad (67)$$

where $\mathbf{v}$ and η are, respectively, the fluid's velocity held and the dynamic viscosity. For an incompressible fluid, the continuity equation is given by

$$\nabla \cdot \mathbf{v} = 0, \quad (68)$$

which is similar to Eq. (65). For slow fluid how, that is, when the Reynolds number $\text{Re} \ll 1$, the nonlinear inertial term, $\mathbf{v} \cdot \nabla \mathbf{v}$, is very small and can be neglected, which means that the Navier-Stokes equations reduce to

$$-\nabla P + \eta \nabla^2 \mathbf{v} + \mathbf{F} = \rho \frac{\partial \mathbf{v}}{\partial t}. \quad (69)$$

Thus, we see that, under steady-state condition, and when the flow of the fluid is slow, the governing equations for the displacement held $\mathbf{u}$ and the velocity held, $\mathbf{v} = \partial \mathbf{u} / \partial t$, are exactly identical, provided that there is a one-to-one correspondence between the shear modulus μ and the dynamic viscosity η .

In addition, under certain conditions, the effective viscosity η of a suspension of completely rigid spheres in creeping (very slow) how of an incompressible fluid of viscosity η_1 is related to the *steady-state* effective shear modulus μ of a two-phase material composed of the same completely

rigid spheres in an incompressible matrix with shear modulus μ_1 . In this case, the working equation is given by

$$\frac{\eta_e}{\eta_1} = \frac{\mu_e}{\mu_1}. \quad (70)$$

Equation (70) is exact when, regardless of the configuration of the particles, hydrodynamic interactions between the particles can be neglected, which is the case when the system is infinitely dilute so that the volume fraction of the particles approaches zero. Even if the system is non-dilute, Eq. (70) would still be exact, provided that the configurations of the particles in the flow and the elasticity problems are identical.

Having established a theoretical connection between the viscosity η of a sol and the shear modulus of an appropriate two-phase material, the one-to-one correspondence between η and the shear modulus of a superelastic percolation network should be clear because,

- (i) η and μ both diverge at p_c (the GP), and,
- (ii) the percolation models predict accurately the structure and elastic moduli of nearly critical gels.

On the other hand, de Gennes (1979) (see also Allain et al. (1991)) suggested an analogy between η and the effective conductivity of a conductor-superconductor percolation networks, the effective conductivity of which diverges at p_c according to power law (42), so that $k = s$.

Extensive experimental data indicate, however, that even a one-to-one correspondence between η and the shear modulus of a superelastic percolation network is not nearly enough to explain the power-law behavior of the viscosity of gelling solutions near the GP. Most of the experimental data for the value of k is either in the range of 0.6–0.9 or in the range of 1.3–1.5. Examples of experimental data for the first group include those reported by Adam et al. (1979, 1985), Allain and Salomé (1987b), and Durand et al. (1987), while Djabourov et al. (1988); Martin et al. (1988), and Martin and Wilcoxon (1988) reported data consistent with the second group.

On the other hand, the power-law behavior of the shear modulus of a 3D superelastic percolation network, as well as a superconducting percolation network, near p_c is characterized by a *unique* exponent S . The reason for two distinct values of k may be (Arbabi and Sahimi 1990b; Sahimi and Arbabi 1993) that the dynamics of the sol solutions that yield the two distinct values of k may be completely different.

In one case, the solution may be close to the Zimm limit in which there is little or no polymer diffusion in the reaction bath, because there are strong hydrodynamic interactions between the monomers, and also between polymers of various sizes, that prevent diffusion, or slow it down significantly, in a nearly critical sol near the GP. Hence, a superelastic percolation network – a *static* system with fixed rigid clusters – may be suitable for simulating such a solution. For this limit, Arbabi and Sahimi (1990b) suggested that,

$$S = \nu - \frac{1}{2}\beta, \quad (71)$$

where ν and β are the standard percolation exponents. Then, with $\nu \simeq 0.89$ and $\beta \simeq 0.41$ for 3D percolation, one obtains $S \simeq 0.68$ for the divergence of the shear modulus of 3D superelastic percolation networks at the percolation threshold, which seems to explain estimates of k for those gelling solutions that have a viscosity exponent in the range of 0.6–0.9.

On the other hand, the gelling solution may also be in, or near, the Rouse regime – one in which there are no hydrodynamic interactions between the polymers of various sizes – and, therefore, the finite polymers can diffuse essentially freely in the reaction bath. To simulate this regime the following model was proposed (Arbabi and Sahimi 1990b; Sahimi and Arbabi 1993): We consider a superelastic percolation network in which every cluster of the totally rigid bonds (the bonds in such clusters are totally rigid in order to distinguish them from those with a finite elastic constant) represents a finite polymer. Due to randomness of percolation networks, there is, of course, a wide distribution of such polymers or clusters in the network. The “soft” bonds –

those with a finite elastic constant – represent the liquid solution in which the rigid clusters move randomly, with equal probability, in any direction, simulating diffusion of the finite polymers in the reaction bath. Two rigid clusters cannot overlap, but can temporarily join and form a larger cluster, which may also be broken up again at a later time. Thus, at every time step, a cluster and a direction for diffusion are picked at random, and the cluster is moved by one step (one lattice bond) in that direction, taking into account the excluded-volume effect. This is then a *dynamic* superelastic percolation network, the shear modulus of which can be calculated at long times. Monte Carlo simulations (Arbabi and Sahimi 1990b; Sahimi and Arbabi 1993) indicated that the shear modulus of such a dynamic superelastic percolation network diverges with an exponent S' , which Arbabi and Sahimi (1990b) proposed it to be given by

$$S' = 2\nu - \beta. \quad (72)$$

Equation (72) predicts that in 3D, $S' \simeq 1.35$, which appears to explain the viscosity exponent for those gelling solutions that have an exponent k in the range of 1.3–1.5.

Daoud (2000) also argued that, similar to the case of the elastic moduli of nearly critical gels described above, one must consider two distinct regimes for explaining the power-law behavior of the viscosity near the GP. According to him, if the elastic chains carry an energy which is of the same order of magnitude as the thermal energy $k_B T$, then the exponent S should be given by Eq. (71). On the other hand, if the elastic chains are stretched and have an extra energy larger than $k_B T$, then one should recover Eq. (72), which had also been conjectured by de Gennes (1979), but based on the analogy between the viscosity and the effective conductivity of superconducting percolation networks described above.

We should point out that, as in the case of the elastic moduli of nearly critical gels discussed earlier, there are some experimental data that indicate some deviations of k from S or S' . As pointed out earlier, however, experimental determination of k (and the elasticity exponent z) involves (see, e.g., Durand et al. 1987) measuring the complex

modulus $G^*(\omega)$ for a series of frequencies ω . But, strictly speaking, the power laws for the elastic moduli of the elastic and superelastic percolation networks are valid only in the limit $\omega \rightarrow 0$, whereas in practice it is essentially impossible to reach such a limit and, therefore, the measured values of k may exhibit some deviations from S or S' . Thus, such deviations are probably due to transient effects that should diminish as very low frequencies are accessed. Let us also mention that, Bergman (Bergman 2002) suggested that, $S = s$, but his suggestion does not seem to be supported by the estimates of the two exponents listed in Table 1. More accurate estimates of the exponents may settle this issue.

Physical Gels: Comparison of Experimental Data with the Percolation Model

In physical gels both inter- and intramolecular bondings are non-covalent. The presence of non-covalent bonding means that their numbers and positions fluctuate with time, as well as temperature, as such bonds are reversible. Moreover, the nature of the (physical) cross-links is not completely understood. In many cases they involve hydrophobic, hydrogen bonding, and electrostatic interactions, the combination of which make gaining a better understanding of the properties of physical gels a very complex problem. This is particularly true for biopolymers.

Two well-known examples of physical gels are gelation of silica particles in NaCl solutions and in pure water (Gauthier-Manuel et al. 1987), and silica aerogels (Woignier et al. 1988). As discussed earlier, the attachment of the particles in such gels is by relatively weak association. The BB forces are important in such gels since if touching particles that form long chains are deformed, they roll on top of one another. Such a motion and the displacement of the centers of any three mutually touching particles create forces that are equivalent to the BB forces.

Despite the many complications, percolation theory seems to be capable of providing rational explanations for the scaling behavior of at least

some of the experimental data for the elastic moduli of physical gels near the GP. For example, measurements (Gauthier-Manuel et al. 1987; Woignier et al. 1988) of the elastic moduli of silica gels and aerogels yielded an estimate of the elasticity exponent, $z \simeq 3.8$, which is in excellent agreement with the critical exponent T for the 3D BB model (see Table 1), as well as with Eq. (60).

On the other hand, measurements by Devreux et al. (1993) indicated a crossover between the prediction of the BB model and another regime with a much smaller value of z . Devreux et al. measured the complex modulus G^* of silica gels formed by hydrolysis and condensation of a silicon alkoxide. For a restricted region near the GP they reported that $z \simeq 2.0 \pm 0.1$, close to the exponent T of the CF percolation (or the conductivity exponent), whereas beyond this region they found $z \simeq 3.6 \pm 0.1$, which is close to the elasticity exponent for the 3D BB model. Devreux et al. interpreted their data for the region near the GP in terms of an analogy between elastic percolation networks and random resistor networks.

Despite their success, there are still many issues to be addressed. There is still doubt as to whether percolation models can explain the behavior of many types of nearly critical gels and branched polymers, particularly biopolymers; see, for example, Ross-Murphy (2007). Several sets of puzzling data on the elastic moduli of critical and nearly critical gels remain to be explained. If there is no unique universality class for the elastic moduli and the viscosity, but there is, instead, a multitude of them, the crossovers between the various universality classes remain to be understood.

Application of Percolation Model to Other Types of Macromolecules

In addition to branched polymers and gels, elastic percolation models have been utilized to explain the mechanical properties of other types of macromolecules. An important class of such materials consists of cells and tissues. Powered by the cytoskeleton that includes an active gel of actin

filaments, cross-links, and myosin molecular motors, cells and tissues exert force on their environment, resulting in dynamic changes in their shapes. The size of the individual motors is very small, only a few nm in size, and the force that they can exert is also very small. Biological cells integrate, however, the activity of an ensemble of motors that produces larger contractile forces on cellular and tissue length scales. Experimental studies have provided evidence that the connectivity of the active networks and its mechanical interaction with the motor activity control the contractile behavior. This suggests that percolation theory can explain at least those aspects of the behavior of such materials that have to do with the connectivity of the active networks (Dasanayake et al. 2011; Sheinman et al. 2012; Wang and Wolynes 2012; Alvarado et al. 2013; Ronceray et al. 2016). Experimental data and percolation models for this very interesting problem have been reviewed by Alvarado et al. (2017).

Another important phenomenon is planar cell polarity. In this phenomenon, a large number of cells become polarized and align in a plane in a coordinated manner. Chandrasekaran and Bose (2019) developed a lattice spin model for the PCP that could produce the alignment of cells through local interactions. In their model alignment of the cells gives rise to the formation of clusters of aligned cells that exhibit percolation transition in terms of their connectivity and formation of a sample-spanning cluster of aligned cells. Chandrasekaran and Bose (2019) showed that their model belongs to the universality class of 2D random percolation.

In addition, percolation, and in particular rigidity percolation, have been used to model and understand the structure of various types of proteins (Deb et al. 2009; Peng et al. 2015; Weber and Pande 2015; Buchholz et al. 2017). Thus, percolation models explain qualitatively, and in many cases quantitatively, the structure, rheology, and mechanical behavior of branched polymers, gels, and other types of macromolecules, particularly biological materials. In particular, such models provide rational explanations for the power-law behavior of many properties of such materials near the percolation threshold, which mean-field theories and effective-medium approximations fail to provide.

Notes added in proof: Very recent large scale simulation of central-force percolation on the BCC lattice by Arbabi and Sahimi (2021) indicated that, as the size of the lattice increases, large fluctuations appear in the elastic moduli of the lattice, and the percolation transition that seem to be a second-order, continuous transition, changes to a discontinuous, first-order one.

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Explosive Percolation Processes

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Article Outline

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Glossary

Achlioptas process A graph evolution algorithm where a fixed number of random choices are considered at each discrete time step, but only the choice that best satisfies a preset criteria is accepted.

Component A set of nodes that can reach one another via a path of edges. The size of a component is the number of nodes it contains.

Discontinuous percolation transition The giant component exhibits a discontinuous jump in size when it emerges.

Giant component A component with size linear with respect to the number of nodes in the network.

Network/Graph A set of nodes (vertices) and links (edges) connecting them.

Percolation phase transition The emergence of large-scale connectivity (a giant component) as link density is increased.

Definition

Explosive percolation (EP) is a general phenomena often resulting as a consequence of delaying the emergence of large-scale connectivity in a

random network or lattice system. The general percolation phase transition (chapter ▶ “[Percolation Phase Transition](#)”) describes the onset of large-scale connectivity among the nodes of a network or sites on a lattice as the density of connections increases. For explosive percolation, one starts from a completely disconnected system and adds connections at random following some fixed algorithm that repeatedly suppresses the onset of large-scale connectivity. In processes that display explosive percolation, the onset can be significantly delayed but, once the percolation transition is inevitably reached, large-scale connectivity emerges drastically, showing a substantial discontinuous jump in any finite system. For some algorithms exhibiting EP, the transition is extremely abrupt yet ultimately continuous in the thermodynamic limit; however, the scaling behaviors in the critical regime are distinct from any previously known universality class. Other algorithms exhibiting EP can be shown to be truly discontinuous transitions in the thermodynamic limit due to underlying mechanisms such as growth by overtaking, correlated percolation, cooperative percolation, and evolution on hierarchical lattices.

Explosive percolation processes, whether continuous or discontinuous, also exhibit a variety of exciting, new phenomena that have yet to be fully understood analytically. For some processes, the supercritical regime is not necessarily described by a function (it is non-self-averaging). For others, there are multiple giant components that coexist in the supercritical region. It is also possible to observe a second phase transition which is discontinuous and arbitrarily close to the initial percolation transition, including a “Devil’s staircase” of supercritical discontinuous phase transitions. Finally, the microscopic patterns of certain EP processes reveal a discrete scale invariance of microtransitions in the early evolution that can provide a recurrence relation for calculating the location of the critical point. This is especially relevant for discontinuous transitions which do not display the scaling properties and fluctuations

that can serve as early warning signals for the onset of continuous phase transitions.

Percolation, in general, serves as a basic underpinning for modeling complex networks (chapter ► “[Percolation in Complex Networks](#)”). With the growing importance of networks in our modern society – from transportation networks to communication networks to online social networks to financial networks – such models are increasingly relevant. Explosive percolation describes the abrupt transition that often results from processes that delay the onset of large-scale connectivity and provides an emerging paradigm for modeling the consequences of interventions to delay phase transitions.

Introduction

Our modern society depends on a collection of interdependent networks, spanning social, biological, and technological systems. These include transportation networks, communication networks, online social networks, financial networks, genetic regulatory networks, metabolic networks, and electric power grids, among others. Thus, understanding the fundamental properties of complex networks, including how their structure and function are intimately related, is of increasing importance. It is also well known that the properties of a network can exhibit phase transitions, such as percolation (chapter ► “[Percolation Phase Transition](#)”) or the emergence of a k -core (chapter ► “[Bootstrap Percolation](#)”), meaning that networks can exhibit sharp changes in their structure and function with the addition or deletion of a few edges.

Percolation, the emergence of large-scale connectivity, has a profound effect on the macroscopic behaviors of a system above and below the critical point, t_c . There are scenarios when ensuring large-scale connectivity is essential. For instance, a transportation network (like the worldwide airline network) or a communication system (like the Internet) is only useful if a large fraction of the nodes can reach one another. Yet, in other contexts, large-scale connectivity is a liability. For instance, above t_c a virus spreading

on a social or computer network can reach an extensive fraction of nodes causing an epidemic outbreak. Below t_c , each outbreak would be contained in a small, isolated cluster. Thus, there is great interest in understanding how to manipulate the location of the percolation transition to either enhance or delay its onset and in understanding the consequences of such interventions.

Here we review explosive percolation (EP), which describes the phenomena that often results from delaying the percolation phase transition. The onset can be significantly delayed, but once the percolation transition is inevitably reached, large-scale connectivity emerges drastically.

Description

Random Graph Models

In its most basic form, a simple network is a collection of nodes together with the edges that link individual pairs of nodes. In mathematics, the term graph is typically used for network, vertex for node, and edge for link. Here, we use the terms interchangeably. See the volume “Complex Networks and Graph Theory” for a discussion of the subtle distinctions between the fields.

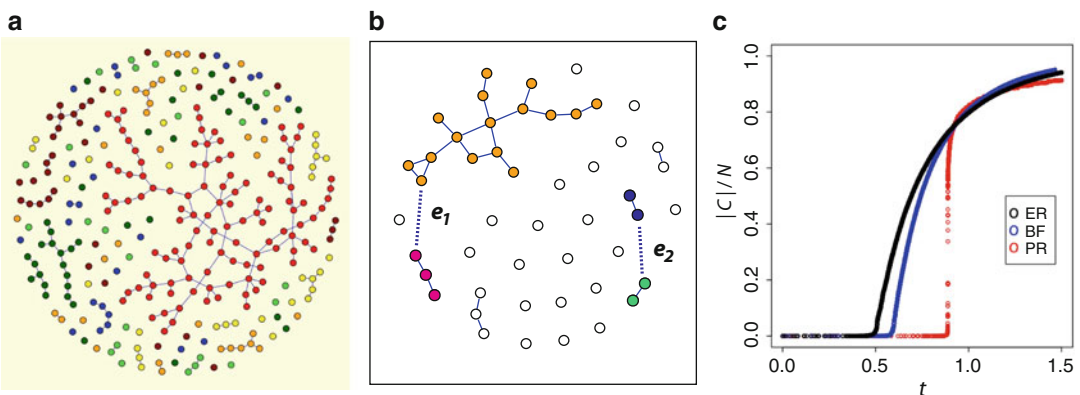
Perhaps the simplest mathematical model of a random network is that developed by Erdős and Rényi in the late 1950s (Erdős and Rényi 1959, 1960) (with a similar model developed independently and contemporaneously by Gilbert (1959)). It is defined as follows: Start from a collection of N initially isolated nodes and then consider each possible edge between two distinct nodes and add that edge with probability p . Here the edges are *undirected*, thus the total possible number of edges is $N(N - 1)/2$, the expected number of edges is $pN(N - 1)/2$, and the edge density (i.e., number of edges per node) is $t = p(N - 1)/2$. We wish to understand properties of the typical graphs parameterized by N and p . Ultimately we are interested in the “thermodynamic limit” $N \rightarrow \infty$, so it is standard to parameterize the system by edge density t . Equivalently, the Erdős-Rényi (ER) model can be formulated as a kinetic process (Ben-Naim and

Krapivsky 2005a): Starting from a collection of N isolated nodes, define a discrete time process where at each time step an edge is chosen uniformly at random from all possible edges and added to the graph. Thus at time step T , the graph will have T edges. The system is still parameterized by edge density $t = T/N$, maintaining $t_c = 1/2$ and the properties discussed above. (Note that the likelihood of sampling the same edge twice for $t < t_c$ decays as $1/N$, thus, when determining the location of the percolation transition, it is irrelevant whether edges are sampled with replacement or not.)

For small values of t , the resulting graph is disjoint, consisting of small isolated clusters (i.e., components) of connected nodes. Each component consists of a group of nodes connected to one another via a path traversing edges (See Fig. 1a for an illustration). These paths allow for interaction among all the nodes in the component, such as passing a message throughout the group or transmitting a disease. Let C denote the largest component and $|C|$ its size (i.e., the number of nodes in the component). There is a sharp transition in $|C|$ at a critical value $t_c = 1/2$. Below t_c , $|C|$ is of order logarithmic in N . Above t_c , there is a unique largest component with size linear in N . Exactly at t_c it is known that $|C|$ is of order $N^{2/3}$ (Bollobás 2001; Durrett 2007).

Achlioptas Processes

At a Fields Institute workshop in 2000, Dimitris Achlioptas introduced a method for extending the Erdős-Rényi random graph process to enhance or delay the onset of the percolation phase transition. His idea exemplifies the “power of two choices,” an innovation used in randomized algorithms (Azar et al. 1994, 1999) that is particularly effective for tasks such as load balancing (Adler et al. 1998; Mitzenmacher 2001). Start from a collection of N isolated nodes, but rather than choosing one edge at random in each discrete time step, choose two candidate edges, denoted $\{e_1, e_2\}$, and examine the consequence of adding each one individually to the graph. The edge which best satisfies a preset selection criteria is added to the graph and the second candidate edge is discarded for this time step. Selection criteria can include keeping components as small as possible (which delays the onset of large-scale connectivity) or, alternately, growing a large component as quickly as possible (which enhances the onset). Note that if the selection criteria were to always keep the first edge, or to always keep the second edge, or to choose between the two candidate edges uniformly at random, this would reduce to the classic Erdős-Rényi process. The process can also be



Explosive Percolation Processes, Fig. 1 (a) A sample network with the nodes in each distinct component rendered in the same color. The largest component, C , is indicated in red. (b) An example of one time step of the Product Rule process. Two edges, e_1 and e_2 , are examined. The product of the components merged by e_1 is 48 and by

e_2 is 4, so e_2 is accepted in and e_1 rejected. (c) Typical evolution of the Erdős-Rényi (ER), Bohman-Frieze (BF), and Product Rule (PR) processes. Plotted is the fractional size of the largest component, $|C|/N$, as a function of edge density t . Figures are reprinted from D’Souza and Nagler (2015)

generalized by considering $m > 2$ candidate edges at each time where m is a constant. A graph evolution algorithm where a fixed number of random choices are considered at each discrete time step, but only the choice that best satisfies a preset criteria is accepted, has become known as an *Achlioptas Process*. When connectivity is the graph property of interest, the synonymous term *competitive percolation process* is also used extensively.

The first Achlioptas Processes to be investigated appeared in the literature in 2001 (Bohman and Frieze 2001) and considered “bounded size” rules where all components of size K or greater are treated equivalently. In this model (introduced by Bohman and Frieze (BF) (Bohman and Frieze 2001)), e_1 is accepted if it joins two isolated nodes (and e_2 is rejected), otherwise e_2 is accepted (and e_1 is rejected). Thus, only components of size one are distinguished, and all components of size $K = 2$ or greater are treated equivalently. Bohman and Frieze showed rigorously that the transition could be delayed but did not investigate the detailed nature of the percolation transition. Bounded size rules are amenable to description as cluster evolution differential equations such as the Smoluchowski coagulation equation (von Smoluchowski 1916; Aldous 1999), which assume that at each discrete time step two independent components are merged. The error in this assumption can be rigorously analyzed and, as a result of detailed analysis, it is conjectured that all bounded size rules lead to continuous phase transitions (Spencer and Wormald 2007).

Achlioptas Processes and Explosive Percolation

Analysis of unbounded component size rules is more elusive and the first study to receive considerable attention appeared in 2009 (Achlioptas et al. 2009). Its focus is on the Product Rule defined as follows: As in any basic Achlioptas Process, two candidate edges $\{e_1, e_2\}$ are chosen uniformly at random. For low edge density (i.e., the sparse regime) and $N \gg 1$, the two edges involve four distinct vertices with high probability. We are interested in the size of the component to which each vertex belongs, denoted $\{|C_a|, |C_b|,$

$|C_c|, |C_d|\}$. Without loss of generality, let e_1 denote the edge which joins the first two components and e_2 the second two. If $|C_a| \cdot |C_b| < |C_c| \cdot |C_d|$, then e_1 is added to the graph. Otherwise, e_2 is added. In other words, we retain the edge that minimizes the product of the two components that would be joined by that edge. See Fig. 1b for an explicit illustration. (Note that the occurrence of vertices a and b , or vertices c and d , that belong to the same component is extremely rare in the regime $t < t_c$ when components are of size $O(\log N)$.)

The process is started from a collection of N isolated nodes, and evolution via the Product Rule occurs at each discrete time step. A typical realization for a system of size $N = 10^6$ is shown in Fig. 1c, which also includes a comparison to a comparable Erdős-Rényi and a Bohman-Frieze (BF) (Bohman and Frieze 2001) realization. Note that the critical point is considerably delayed for the Product Rule and that, when large-scale connectivity does ultimately emerge, it increases drastically, going from sublinear to a level approximately equal to the corresponding Erdős-Rényi and BF processes during an almost imperceptible change in edge density.

As rigorous analysis of the Product Rule remains an open challenge, the 2009 study focused on direct simulation of the process (Achlioptas et al. 2009). To quantify the abruptness of the connectivity transition, the scaling window as a function of system size N , denoted $\Delta_N(\gamma, A)$, was analyzed. Explicitly, this is the number of edges that must be added during the interval starting from the last edge for which $|C| \leq \lfloor N^\gamma \rfloor$ and ending with the first edge for which $|C| \geq \lfloor AN \rfloor$. Choosing $\gamma = 1/2$ ensures the scaling window begins before the onset of the Erdős-Rényi transition (which has $|C| \sim N^{2/3}$ at t_c). Choosing $A = 0.5$ ensures that the majority of the vertices belong to C by the end of the window. If $\Delta_N(\gamma, A)$ increases sublinearly with N , for instance, if $\Delta_N(\gamma, A) \propto N^b$ with $b < 1$, then $\Delta_N(\gamma, A)/N \rightarrow 0$ as $N \rightarrow \infty$. In other words, the increase in edge density necessary for C to go from size N^γ to size AN approaches zero, providing strong evidence that large-scale connectivity emerges in a discontinuous phase transition. Systems up to size $N \sim 6 \times 10^7$ were studied by Achlioptas et al. (2009), and the results indicate a

sublinear scaling window for the Product Rule of the form $\Delta_N \propto N^b$, with $b \approx 2/3$ and critical edge density $t_c \approx 0.888$. For Erdős-Rényi, the scaling window is linear in system size ($b = 1$) and recall that $t_c = 0.5$.

The publication of Achlioptas et al. (2009) led to a flurry of research analyzing the Product Rule on different underlying substrates. These include the Product Rule on a lattice (Ziff 2009) and on networks with power-law degree distributions (i.e., scale-free networks (chapter ► “Percolation in Complex Networks”)) (Radicchi and Fortunato 2009; Cho et al. 2009). These studies provided similar evidence that the Product Rule leads to a discontinuous percolation transition, yet, they also highlighted the additional existence of scaling behaviors characteristic of second-order phase transitions (Ziff 2010; Radicchi and Fortunato 2010). Many other fixed choice Achlioptas Processes have now been analyzed, such as rules using the sum rather than product, rules allowing for $m > 2$ choices (i.e., “best of m ” rules), and “triangle rules” that consider the candidate edges between three vertices which requires analyzing only three components (rather than the four components required for two independent edges) (Friedman and Landsberg 2009; D’Souza and Mitzenmacher 2010; Riordan and Warnke 2012a). Similar results of sublinear scaling windows and critical scaling behaviors are observed (see Bastas et al. 2014 for a review of many of these processes). (Note that hybrid, mixed behaviors had been previously established for several models of “jamming percolation” on low-dimensional lattices which incorporate spatial correlations intended to capture glassy dynamics in materials. Such models exhibit a discontinuous jump in an order parameter but diverging length scales characteristic of second order transitions (Schwarz et al. 2006; Toninelli et al. 2006; Jeng and Schwarz 2010; Cao and Schwarz 2012).)

An important step in clarifying the nature of these competitive percolation transitions was a study by Nagler et al. considering the impact of a *single* edge (Nagler et al. 2011) which provides a more crisp analysis than that allowed by the scaling window. It was shown that, for the Product

Rule and similar models, the maximum change in size of the largest component from the addition of a single edge (denoted $\Delta C_{\max}$) decays as a power law with system size, becoming ultimately continuous at extremely large length scales (Nagler et al. 2011; Manna and Chatterjee 2011). The rate of decay is typically quite small: for the Product Rule, $\Delta C_{\max} \sim N^{-0.065}$. (See the associated discussion in section “Applicability to Real-World Networks” on crossover lengths which can be greater than 10^{18} .)

Mounting numerical evidence and heuristic arguments indicated that Achlioptas Processes lead, in fact, to continuous phase transitions (da Costa et al. 2010; Grassberger et al. 2011; Lee et al. 2011; Tian and Shi 2012) but with a universality class distinct from any previously observed (Grassberger et al. 2011; Tian and Shi 2012). Finally, in 2011 a rigorous proof by Riordan and Warnke showed that any Achlioptas Process (with a fixed number of choices) leads to a continuous percolation transition (Riordan and Warnke 2011). They proved, in essence, that the number of subcritical components that join together to form the macroscopic-sized component that emerges is not subextensive in system size. In the words of Friedman and Landsberg, the Product Rule does not lead to the buildup of a “powder keg” (Friedman and Landsberg 2009). Yet, Riordan and Warnke showed that if the number of choices m is allowed to increase just slightly with system size N , so that $m \rightarrow \infty$ as $N \rightarrow \infty$ (for instance, $m \sim \log(\log N)$), then this is sufficient to allow for a truly discontinuous transition.

Novel Supercritical Properties

Achlioptas Processes (whether fixed or infinite choice) display novel supercritical properties.

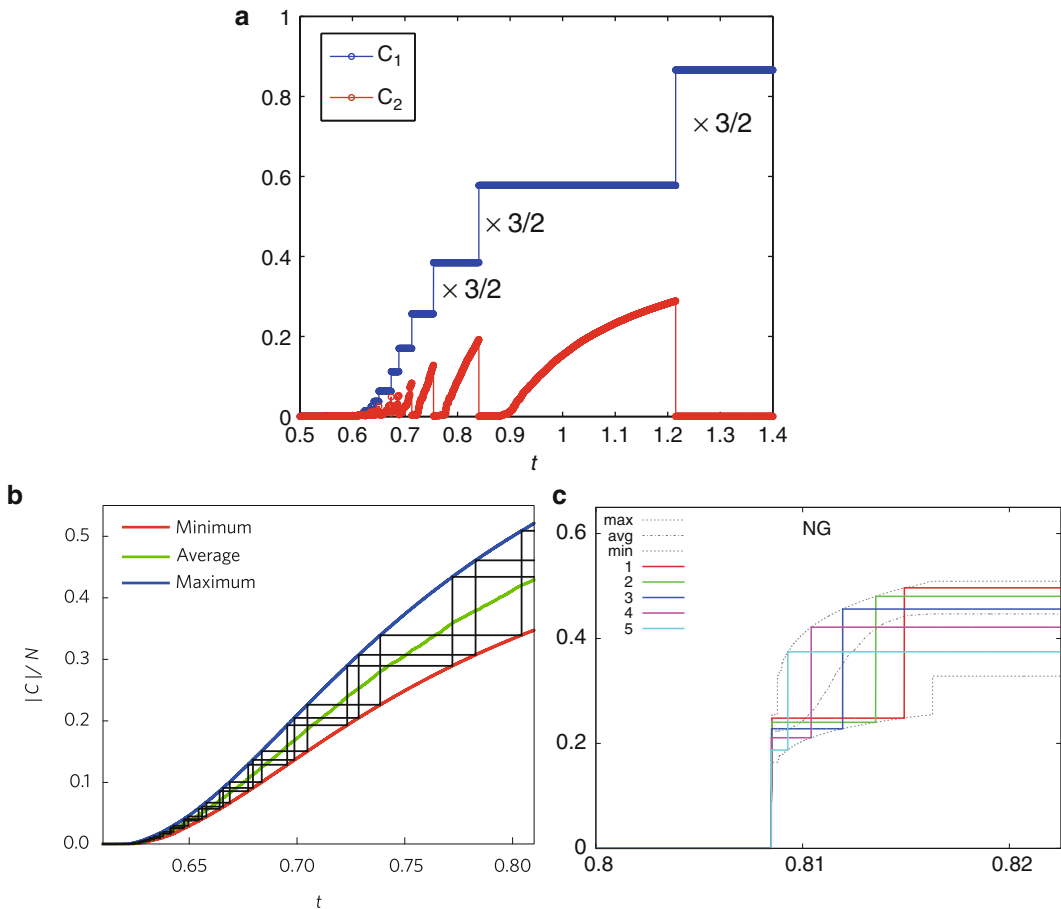
Nagler, Tiessen, and Gutch showed that a fixed choice Achlioptas Process can be continuous in the sense defined by Riordan and Warnke (2011) yet exhibit infinitely many discontinuous jumps, with the first such jump within arbitrary vicinity of the initial percolation transition (Nagler et al. 2012; Schröder et al. 2013). For the model studied in Nagler et al. (2012), the jumps follow a Devil’s staircase ordering (see Fig. 2a). Most importantly, they show that continuity at the first

connectivity transition and discontinuity of the percolation process can be compatible (Nagler et al. 2012). See Chen et al. (2013a) for additional models now known to similarly exhibit a host of discontinuous jumps after an initial smooth percolation transition. See Schröder et al. (2013) and section “Applicability to Real-World Networks” below for connections between the discontinuous supercritical jumps and crackling noise such as Barkhausen noise in ferromagnets.

From a different perspective, Riordan and Warnke showed that, for fixed choice rules, different realizations of the process may have

tremendous variation from one another in the supercritical regime (Riordan and Warnke 2012a), as shown in Fig. 2b and c. In such cases, the system is not self-averaging and the realizations do not converge to a function (Riordan and Warnke 2012a); the supercritical behavior cannot be described analytically. In more recent work, Riordan and Warnke make progress on establishing convergence of Achlioptas Processes in the subcritical regime (Riordan and Warnke 2014).

Several models related to those discussed above have now been shown to exhibit truly



Explosive Percolation Processes, Fig. 2 Achlioptas Processes display novel supercritical properties. (a) A “Devil’s staircase” of discontinuous jumps for the model analyzed in Nagler et al. (2012). Shown are the fractional sizes of the two largest components as a function of the edge density t . (b) and (c) show that Achlioptas

Processes can be nonconvergent (also called non-self-averaging). Figure (b) shows several realizations of the Devil’s staircase process (reprinted from D’Souza and Nagler (2015)) and (c) shows several realizations of the “Nagler Gutch” (NG) process (reprinted from Riordan and Warnke (2012a))

discontinuous percolation transitions. For discontinuous transitions, multiple giant components can coexist in the supercritical region (Chen and D'Souza 2011). At times the coexistence is unstable, leading to a host of additional discontinuous transitions (Chen et al. 2013a). See section “Truly Discontinuous Processes” and references Chen et al. (2013a, b) for examples and more details.

Applicability to Real-World Networks

As mentioned in the Introduction, there is a pressing need to understand the behaviors of networks, and random graphs provide useful modeling tools. For instance, the percolation threshold provides a heuristic lower bound for the onset of an epidemic threshold. One may expect similar benefits by connecting the results obtained for explosive percolation to real-world systems. A first challenge is theoretical and concerns the applicability of the thermodynamic limit to real-world networks. A second challenge is more practical and concerns which real-world systems can be modeled with these processes.

The Thermodynamic Limit

With regard to the first challenge, the rigorous proof by Riordan and Warnke (2011) shows that in the limit $N \rightarrow \infty$ to the scaling window is linear in system size N , but numerical evidence on systems up to size $N \sim 10^7$ indicates the window is sublinear (Achlioptas et al. 2009). Thus, there must be a crossover length N^* where the system size becomes large enough that actual realizations show convergence to the asymptotic limiting behavior. A method for estimating the crossover length is to model the expected evolution of a network using cluster aggregation differential equations, such as the Smoluchowski coagulation equation (von Smoluchowski 1916; Aldous 1999), which is a “mean-field” analysis over the ensemble of all possible random graphs. See Aldous (1999) for a discussion of convergence and concentration assumptions underlying this approach. A second assumption is that two independent clusters are merged at each discrete time step. In Spencer and Wormald (2007), this source of error is analyzed for a bounded size rule process. Cluster aggregation approaches to general

percolation provide useful analytical tools (Ben-Naim and Krapivsky 2005a; Krapivsky et al. 2010), which have been quite conducive for modeling explosive percolation processes (D'Souza and Mitzenmacher 2010; Manna and Chatterjee 2011; Cho et al. 2010).

Da Costa et al. (2010) analyze cluster aggregation models related to the Product Rule and show that the largest component obeys a scaling relation $|C|/N \sim (t - t_c)^\beta$ for t just above t_c . Via numerical iteration of their system of equations, they determine $\beta = 0.0555$, indicating unusually rapid, albeit continuous, growth (For Erdős-Rényi the “mean-field” exponent $\beta = 1$ is obtained.). Using the scaling relation, we can calculate the maximum impact from the addition of a single edge, which has a corresponding change in edge density $\Delta t = 1/N$. For $t < t_c$, by definition $|C|/N \rightarrow 0$. As we pass into the critical regime $|C|/N \sim (\Delta t)^\beta = (1/N)^\beta$. This means that, for a system of size $N = 10^{1/\beta}$, the addition of a single edge causes the order parameter to exhibit a discrete jump equal to 10 % of the system size, $\Delta |C|/N = 0.1$. For a process with $\beta = 0.0555 \approx 1/18$, the crossover length is $N^* > 10^{18}$. The thermodynamic limit is extremely relevant when considering phase transitions in physical materials, where system sizes are on the order of Avogadro's number, $N \sim 10^{23}$. But real-world networks, such as the Internet, the worldwide airline network, online social networks, gene interaction networks, etc., are all considerably smaller than 10^{18} . Although fixed choice Achlioptas Processes yield continuous transitions in the thermodynamic limit, such processes yield significant discrete jumps in the realm of real-world networks.

Applicability to Modular Networks

A more practical issue is identifying how explosive percolation can be useful for modeling real-world networks. Two studies (Rozenfeld et al. 2010; Pan et al. 2011) show that the paradigm can be useful for modular networks (also known as networks with strong “community structure” (“Community Structure in Graphs”)). Rozenfeld et al. (2010) consider an evolutionary process on the human protein homology network. The general belief is that proteins evolve via duplication-mutation events

from ancestral proteins, and it has been shown that more similar (i.e., homologous) proteins organize into network modules (Medini et al. 2006). Using data on the human protein homology network, Rozenfeld et al. consider an evolutionary process initialized with all the proteins disconnected and with edges between the most similar proteins added sequentially. This leads to the emergence of many large isolated components of tightly connected nodes, which eventually link together with the addition of just a few intercomponent edges so that global connectivity emerges in an explosive manner. As the authors remark, the emergent structure is similar to the dense connectivity within a community and the weak links between communities suggested by Grannoveter for social systems (Granovetter 1973).

Pan et al. show in their study (Pan et al. 2011) that monitoring the evolution of an explosive percolation process on a network reveals information about the underlying structure. They consider empirical data from two real-world social networks: one is a mobile phone call network, and the other is a coauthorship networks of scientists. Initially, all the empirical edges are considered “unoccupied” and an Achlioptas Process is used to sequentially “occupy” edges. They show that, at t_c , the component structure reflects the underlying community structure of the network. Thus, applying such graph evolution processes to data from real-world networks can provide a potential tool for uncovering unknown, underlying structures.

Applicability to Materials

Standard formulations of percolation have been used to model many properties of materials, such as electrical and thermal conductivity, flow through porous media, and polymerization (chapter ► “Percolation Phase Transition”). Such formulations are particularly effective at modeling properties of disordered media. But, as discussed in detail in section “Truly Discontinuous Processes” below, explosive percolation offers a novel ingredient, namely, suppressing the growth of the largest components and instead creating many components of uniform size. This allows us to extend percolation models to systems that

have not been previously amenable to such treatment.

For example, consider the seminal model of diffusion-limited cluster aggregation (Witten and Sander 1981). Here clusters move via Brownian motion so that the velocity of a cluster is inversely proportional to the square root of its size and thus larger clusters move considerably more slowly. Cho and Kahng (2011) show that diffusion-limited cluster aggregation can be mapped onto the framework of explosive percolation. They consider clusters moving on an underlying two-dimensional lattice via Brownian motion, and whenever two clusters become nearest neighbors, they merge into one larger cluster. Here the number of aggregation events is regarded as the number of edges. They show that Brownian motion suppresses of the mobility of the largest clusters, impeding their growth, and leading to the discontinuous emergence of a giant cluster as a function of edge density. They also consider a generalized Brownian motion where the velocity is inversely proportional to the mass of the cluster to a power η and map out the tricritical point separating discontinuous from continuous emergence as a function of η .

Schröder et al. (2013) study a model of explosive percolation where the merging of components with substantially different sizes is systematically suppressed. They show that this leads to a series of multiple discontinuous jumps in the supercritical regime. The sizes and locations of the jumps are randomly distributed, similar to crackling noise observed in materials, such as when a sheet of paper is crumpled. Their framework links explosive percolation with phenomena that exhibit crackling noise, are non-self-averaging, and exhibit power-law fluctuations such as Barkhausen noise in ferromagnets.

A different system that also maps onto the explosive percolation framework involves collections of nanotubes. In general, the emergence of percolating paths in bundles of nanotubes captures the transition from insulator to conductor and plays a fundamental role in the design of nanodevices (Kim et al. 2010). This is typically modeled as ordinary percolation, but, Kim et al. (2010) show that explosive percolation

processes are more realistic models as observations of real-world systems show that the sizes of the bundles are uniform. Similar to explosive percolation processes (and unlike regular percolation), the growth of larger bundles is suppressed and the transition becomes extremely abrupt. The transition shows hysteresis, as is expected for first-order transitions (Kim et al. 2010).

Modeling the Consequences of Repeated Small Interventions

Explosive percolation has also been proposed as a paradigm for modeling modern engineered and financial systems, where small patches are often applied to postpone the occurrence of catastrophic events, such as the breaking of a dam or crashes in financial markets and economies (ETH Risk Centre 2012; Helbing 2013). Other potential applications are discussed in section “Further Directions.”

Truly Discontinuous Processes

For graph evolution via an Achlioptas Processes, the weak constraint that the number of choices $m \rightarrow \infty$ as $N \rightarrow \infty$ is sufficient to allow for a discontinuous percolation transition. Yet, on a lattice, an Achlioptas Process with a fixed number of choices can yield a discontinuous transition. Percolation on a lattice (chapter ► “Efficient Simulation of Percolation Lattices”) is often measured by the emergence of a spanning cluster – a path of activated links that connect sites from one side of the lattice to another in the limit when the lattice size $L \rightarrow \infty$. Cho et al. (2013) show that the emergence of a spanning cluster under an Achlioptas Process with a fixed number of choices m can be discontinuous for a lattice with dimension $d < d_c = 6$ as long as $m > m_c = d/(d - d_{\text{BB}})$, where d_{BB} is the fractal dimension of the “backbone” (which they calculate analytically and measure numerically). When $d = 2$, $m_c \approx 2.554$ so setting $m = 3$ is sufficient for a discontinuous transition. For $d > d_c$, the transition will be continuous for any constant choice of m . It may prove illuminating to analyze the tricritical point (separating the continuous and discontinuous regimes as a function of m for $d < d_c$), as has been done recently for other percolation models that

exhibit discontinuous and continuous regimes (Cao and Schwarz 2012; Cho and Kahng 2011; Araújo et al. 2011; Cellai et al. 2011).

It is worthwhile to note that Erdős-Rényi percolation can be considered a form of “gravitational coalescence” between components. Under the kinetic formulation, at each discrete time step two vertices are chosen uniformly at random and linked by an edge that is added to the graph. The probability that a randomly chosen vertex is in a particular component of size j is j/N . Thus, to first order, the probability that a randomly selected edge merges a particular component of size j with one of size i is proportional to ij/N^2 . (We have neglected the probability that both vertices belong to the same component, but this is negligible in the subcritical regime; See Aldous (1999) for more rigorous details.) As with gravitational attraction, the force between two bodies (i.e., components) is proportional to the product of their masses (More precisely this is termed “multiplicative coalescence” (Aldous 1999)). It suffices to say that, under Erdős-Rényi evolution, the largest components quickly merge together to form one larger component, hence amplifying the likelihood of that component being included in subsequent edges. Such arguments provide the intuition for why there is only one unique giant component in the supercritical regime for Erdős-Rényi percolation.

The publication of Achlioptas et al. (2009) led to increased activity in the field and to the discovery of several random graph percolation models that exhibit truly discontinuous transitions. These models break the gravitational coalescence seen in Erdős-Rényi allowing instead for a multitude of components with sizes similar to that of the largest component. This creates the necessary “powder keg” (Friedman and Landsberg 2009) in the subcritical regime, and can allow for multiple, coexisting giant components in the supercritical regime (Chen and D’Souza 2011). (The “powder keg” is, in essence, a collection of components which contain cn nodes in total where the sizes of the components diverge to ∞ as $N \rightarrow \infty$ for some constant c . The merging of the components in the powder keg leads to the discontinuous percolation transition.)

Two of these models (Chen and D’Souza 2011; Araújo and Herrmann 2010) work by suppressing the growth of the largest component. The model introduced in Araújo and Herrmann (2010) considers a regular lattice as the underlying substrate with a single edge examined at a time (i.e., $m = 1$). If a randomly chosen edge would not increase the current size of the largest component, then it is accepted. Otherwise it is rejected with a probability function that decays as a Gaussian distribution centered on the average cluster size. Thus, components that are similar in size to the average are favored. Clear signatures of a first-order transition are observed, such as bimodal peaks for the cluster size distribution (indicating the coexistence of percolative and nonpercolative states in finite systems at t_c).

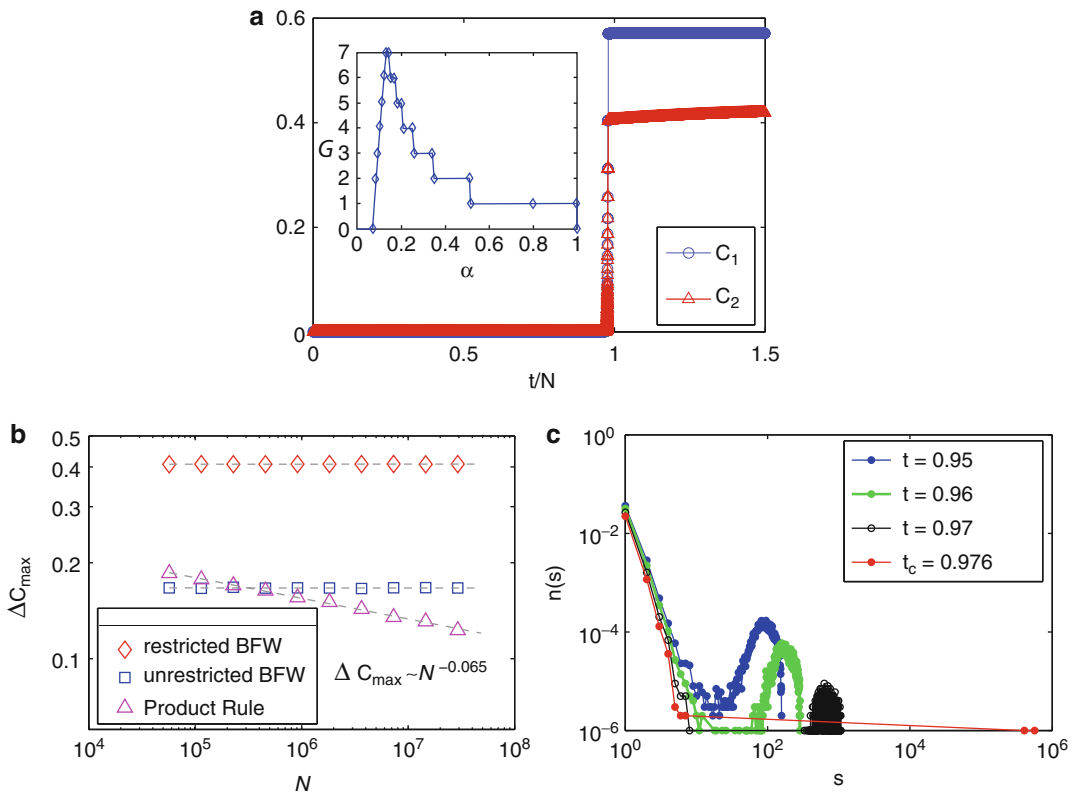
In Chen and D’Souza (2011), a model previously introduced by Bohman, Frieze, and Wormald (BFW) (Bohman et al. 2004) is analyzed. The model considers a single edge at a time. The edge is added to the graph if it participates in a component smaller than some specified size k . Otherwise, the edge is rejected provided that a stringent lower bound on edge density is satisfied throughout the process. If the edge cannot be simply rejected, then the cap k is increased incrementally while the lower bound is correspondingly decreased as a function of k until reaching an asymptotic limiting value, α . In the original model $\alpha = 1/2$ (Bohman et al. 2004) (i.e., asymptotically one half of all edges must be accepted). Chen and D’Souza (2011) show that this process leads to a truly discontinuous transition in which multiple giant components emerge simultaneously, as illustrated in Fig. 3a. Once in the supercritical regime, any edge leading to an increase in the cap size k can be simply rejected and thus the multiple giant components coexist without merging. One can tune the number of coexisting giant components by varying α , as shown inset to Fig. 3a. The maximum impact from a single edge is shown in Fig. 3b as well as the fact that it is invariant with N for BFW but decays with N for the Product Rule. The evolution of the component size distribution as edge density increases is shown in Fig. 3c, illustrating the buildup of the “powder keg” for the BFW

model. Here $n(s)$ denotes the number of components of size s divided by N . See Chen and D’Souza (2011) for more details and for a complete description of the BFW algorithm.

Although the description of the BFW process is intricate, it gives rise to a simple mechanism as shown in Chen et al. (2012). The largest component cannot grow directly in any significant way (in stark contrast to gravitational coalescence). Instead, the size of the largest component only changes when two smaller components merge together becoming the new largest component. The identity of the giant component changes and all significant growth happens through overtaking (Chen et al. 2012). This is consistent with a theoretical proof by Nagler et al., showing that if the probability of direct growth of the largest component is zero, then this leads to a truly discontinuous percolation transition (Nagler et al. 2011).

Other models that have been shown to lead to discontinuous percolation transitions on random graphs include a restricted Erdős-Rényi process, where one end point of the edge is chosen uniformly at random and the other is chosen randomly from a restricted set (Panagiotou et al. 2011). Ordinary percolation on a hierarchical network can yield a discontinuous percolation transition (Boettcher et al. 2012). Furthermore, there is a Hamiltonian formulation that connects evolution via Achlioptas Processes with an equilibrium statistical mechanics process (Moreira et al. 2010). It was also shown recently that modeling cascading failure on interacting networks via percolation can lead to a discontinuous transition (Buldyrev et al. 2010). Although percolation considers the evolution of the network structure, explosive percolation has also motivated exploration of explosive transitions in dynamical processes taking place on a fixed network structure, such as “explosive synchronization” (Gómez-Gardeñes et al. 2011) in a network of oscillators when the natural frequency of each oscillator is positive correlated with its degree.

Of course, there have long been specialized models of percolation which show discontinuous transitions, such as k -core percolation (chapter ▶ “Bootstrap Percolation”) and the models of jamming on low-dimensional lattices (Schwarz et al. 2006; Toninelli et al. 2006; Jeng and



Explosive Percolation Processes, Fig. 3 (a) Multiple giant components, C_1 and C_2 , arise simultaneously for the BFW process. Inset shows the number of stable giant components, G , as a function of α , the asymptotic fraction of edges that must be accepted (Chen and D’Souza 2011). (b) The maximum impact from a single edge $\Delta C_{\max}$ is invariant with system size N for the BFW process, but decays slowly, as $N^{-0.065}$, under the Product Rule. (The

restricted BFW process requires that each added edge merges two previously distinct components, leading to a bigger discontinuous jump than without the restriction.) (c) Evolution of the component size distribution, $n(s)$, under the BFW process, showing the buildup of the “powder keg” which merges to become two coexisting giant components at t_c . Figures are reprinted from D’Souza and Nagler (2015)

Schwarz 2010; Cao and Schwarz 2012) mentioned in section “Achlioptas Processes and Explosive Percolation”. Mechanisms underlying these processes are primarily cooperative interactions (Bizhani et al. 2012) and correlated percolation (Cao and Schwarz 2012) (the latter in particular on lattices). References (Cao and Schwarz 2012; Bizhani et al. 2012) include interesting discussions connecting these known models to the more recent work on explosive percolation, highlighting lattice models, generalized epidemic models, and the statistical mechanics of exponential random graph models (chapter “Social Networks, Exponential Random Graph (p*) Models for”).

More Developments

A strict scaling theory for a wide class of Achlioptas Processes has been developed producing the full set of scaling functions and critical exponents (da Costa et al. 2014). This work uses the cluster evolution differential equation approach discussed above. In addition, the necessary conditions that a cluster merging process must satisfy to produce a discontinuous percolation transition were established (Cho and Kahng 2014). The key ingredient involves symmetry breaking during cluster merging.

Cluster evolution equations also allow us to study Achlioptas Processes on growing networks. Note that in all the percolation models discussed

thus far, N is fixed and the graph evolves via edge arrival. In a seminal study appearing in 2001, the impact of node arrival on the Erdős-Rényi process was analyzed (Callaway et al. 2001). Starting from a few seed nodes, a new node arrives at each discrete time step and, with probability $\delta \leq 1$, an edge selected uniformly at random is added to the graph. This leads to an infinite order percolation transition (Callaway et al. 2001). Following the same procedure, but using an Achlioptas Process for edge addition, considerably delays the onset of the percolation transition but retains the remarkably smooth, infinite order transition (Vijayaraghavan et al. 2013). Thus, network growth via node arrival allows for a significantly delayed percolation transition yet can mitigate the abrupt, explosive nature that typically results from delay interventions.

The microscopic patterns in the early evolution of percolation processes can be used to predict the location of the critical point (Chen et al. 2014). It is well known that large fluctuations in the relative variance over an ensemble of realizations are typically observed in the critical window during continuous phase transitions. However, Chen et al. (2014) show that such fluctuations can be observed in the early evolution of percolation processes as t increases. In particular, the BFW process exhibits peaks in relative variance at well-defined values of t , and the subsequent peaks obey a discrete scale invariance from which a scaling relation can be derived and the critical point t_c calculated.

The field of percolation is very active and many additional works of note are not discussed in this short Encyclopedia entry, which is intended to provide a basic overview of explosive percolation processes. Some additional models are discussed in the reviews on this topic by Bastas et al. (2014) and by D'Souza et al. (2019).

Future Directions

There are many directions for future work on the topic of explosive percolation, ranging from the more theoretical and mathematical considerations to the more practical aspect of how these processes can help us model and understand real-

world systems. One direction is how explosive percolation processes can be used for creating and analyzing modular networks, as demonstrated by the initial studies in this area (Rozenfeld et al. 2010; Pan et al. 2011). Ordinary percolation on hierarchical lattices leads to an explosive percolation transition (Boettcher et al. 2012) and may also show interesting connections to community structures and clustering phenomena. There is also very limited work concerning explosive percolation on directed networks with the work thus far focused on Achlioptas Processes with fixed choice (Squires et al. 2013) and on rank-ordered networks (Waagen et al. 2017).

A more novel consideration is the range of supercritical properties observed in a variety of EP processes, such as multiple giant components, multiple phase transitions, and the lack of convergence. Some mechanisms that yield explosive percolation (e.g., growth by overtaking) lead to one phase transition and stable coexisting giant components. Yet, other mechanisms result in unstable coexistence and a family of discrete transitions following the initial percolation transition. Moreover, the mere existence of multiple giant components arising from percolation is surprising (Spencer 2010), given the gravitational attraction underlying classic percolation processes such as Erdős-Rényi. Understanding which mechanisms lead to stable and unstable coexisting giants may provide insight into the evolution of modular networks, such as social networks, and also provide a potential mechanism for controlling gel sizes during polymerization when multiple disconnected polymer gels can be desirable (Ben-Naim and Krapivsky 2005b). As discussed in section “[Applicability to Real-World Networks](#)”, explosive percolation can be used to model diffusion-limited cluster aggregation and properties of nanotubes and nanowires. Pushing these models further could provide deeper understanding of these important real-world systems. From a more theoretical perspective, the issue of nonconvergence and lack of self-averaging in the supercritical regime that are observed for many EP processes challenge our current notions of percolation. Furthermore, even for evolution under the specific choice of the Product Rule there remain many open questions as detailed in (Riordan and Warnke 2012b, 2014).

From a conceptual perspective, the insights gained from explosive percolation processes may help us understand how to better manage networks. With our increasing reliance on interdependent systems of networks, from electric power grids to computer networks to transportation networks and global financial networks, there is increasing need to understand the systemic risk underlying these engineered networks. Often human operators or regulators intervene with a network's functions or structure in an attempt to delay an undesirable outcome, such as a leak in a dam or a crash in a financial market. Explosive percolation processes provide a new paradigm for modeling the consequences of repeated, small interventions intended to delay a catastrophe (New views on extreme events: Coupled Networks, Dragon Kings and Explosive Percolation 2012; Helbing 2013).

The fields of percolation and explosive percolation are extremely active with many open questions and new results appearing continually. For a review of recent advances and challenges in the field of percolation, see Araújo et al. (2014). For a review highlighting additional models displaying explosive percolation, see Bastas et al. (2014). For a comprehensive review of explosive phenomena on complex networks, including explosive synchronization, see D'Souza et al. (2019).

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Percolation in Complex Networks

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Glossary

Component The set of nodes reachable from a given node. The nodes of a component are all reachable from each other.

Degree Number of edges emanating from a node.

Giant component The component of a graph with size (number of nodes) of order of the number of nodes in the graph.

Graph A set of nodes (sites) and edges (links or bonds) connecting them.

Loop A path that start and ends at the same node.

Minimum spanning tree In a weighted graph – the tree subgraph of the graph with the minimum total weight.

Optimal path In a weighted graph – the path with minimum total weight connecting two nodes.

Percolation theory The theory studying the connectivity behavior of networks when a fraction

of the nodes or edges are removed. Site (or node) percolation involves occupying a fraction, p , of the nodes of the graph, or alternatively, removing a fraction $q = 1 - p$. In bond (or edge) percolation edges are occupied, or removed, with some probability. A combined site-bond percolation, where both processes occur simultaneously, is also considered.

Percolation threshold The fraction, p_c of occupied nodes or edges, under the graph is fragmented into small components, and above which a giant component emerges.

Random graph A graph selected from an ensemble (probability space) of graphs.

Scale free network A network whose nodes' degrees are distributed according to a power law.

Shortest path The path with minimum number of edges connecting two nodes.

Tree A connected graph (a graph consisting of a single component) with no loops.

Weighted graph A graph where each edge is assigned a (usually non-negative) weight.

Definition of the Subject

In this chapter we survey the application of percolation theory to several random network classes, and in particular, to scale free networks. We show how ideas from percolation theory can be applied to the study of robustness and vulnerability of random networks. We show how percolation techniques can be applied also to understand phenomena such as immunization and epidemic spreading in populations and computer networks, minimum spanning trees and communication paths and fragmentation in social networks.

Introduction

In recent years considerable interest has been given to real world networks. The importance of technological networks such as the Internet and WWW, as

well as the availability of large scale data sets on social, biological and technological networks made this subject approachable and popular.

The main model used in the study of complex networks was Erdős-Rényi (ER) random graphs (Erdős and Rényi 1959, 1960, 1961) (also presented earlier by Rapaport (1957)), which are graphs having N nodes (that is, sites or entities) and M edges (links, or connections between the nodes) distributed randomly between them, or alternatively, the almost identical model, having every pair of nodes connect with a constant probability. One of the key discoveries in recent years was that many real world networks, including the Internet, WWW and many biological and social networks, are not described well by the ER model (Albert and Barabási 2002; Dorogovtsev and Mendes 2003; Newman 2003; Pastor-Satorras and Vespignani 2003). One of the first deviations from the model to be noticed was the tendency of many real world networks to have high clustering (Newman 2003), i.e., neighbors of the same node tend to connect between them (i.e., share an edge). This discovery has lead to the presentation of the small world model (Watts and Strogatz 1998).

The small world model is based on some lattice, such as a one-dimensional ring or a higher dimensional grid, in which rewiring occurs. Some (usually small) fraction, φ of the links in the lattice are removed, and instead, new links are added randomly between the nodes. When φ is moderately small the generated graphs have the desired properties of high clustering, while the average distance between nodes is small (of the order $\log N$), as in random graphs (as opposed to $N^{1/d}$ as in a d -dimensional grid).

The second deviation to be noticed was the deviation of the degree sequence from the expectation of random graph theory. The degree of a node is the number of links (or edges) emanating from it, i.e., the number of neighbors it has in the graph. The number of nodes of degree k in a graph will be denoted $n(k)$, and the degree distribution, i.e., the probability that a random node has degree k , is $P(k) = n(k)/N$. In an ER random graph the expected degree sequence is a Poisson distribution (Bollobás 1985), $P(k) = e^{-C} C^k/k!$, where $P(k)$ is the probability of a node to have degree k , and

c is the average degree ($C = 2M/N$). In many real world networks, including the Internet and WWW, it was observed that the degree distribution is actually a power law,

$$P(k) = ck^{-\gamma}, \quad m \leq k \leq U, \quad (1)$$

where c is a normalization factor, m and U are the minimum and maximum degrees, respectively, and γ is some exponent characterizing the distribution. In most networks studied γ has been found to lay in the range $2 < \gamma < 3$ (Albert and Barabási 2002; Dorogovtsev and Mendes 2003; Newman 2003; Pastor-Satorras and Vespignani 2003). These networks have become known as scale free networks, due to the lack of typical scale for the degree distribution. It should be noted that while m must be supplied externally for the distribution to be normalizable, U can be omitted, and will be determined naturally as the extreme value statistics of N variables, which gives $U \sim mN^{1/(\gamma-1)}$ in this case (Cohen et al. 2000).

Several models have been developed for the understanding and study of scale free networks. The question of the reason for these networks' formation has been addressed by the Barabási-Albert model (1999). Many variants on the model have been studied since (see, e.g., Krapivsky and Redner 2002). Here we will focus on the configuration model, or the generalized random graph model (Bollobás 1980), which is an equilibrium model for random graphs with a given degree distribution, producing all graphs having a given degree distribution with uniform probability. The model starts by having N distinct nodes and randomly selecting the degree of each of these nodes from the given degree distribution. Each node, i is then fitted with k_i "stubs", where k_i is its degree, drawn from the distribution $P(k)$. After all nodes' degrees have been selected, a random matching of the stubs is selected, by choosing random pairs of stubs and pairing them (i.e., connecting the nodes by an edge and removing both stubs) until no stubs are left. In some cases a single stub is left, and also there may be edges connecting a node to itself or more than one edge connecting a given pair of nodes. These cases can be safely ignored as they only have a small effect on the final graphs obtained.

Percolation Thresholds and Network Robustness

One of the fundamental questions regarding a network's structure is its connectivity properties, i.e., what are the properties of the distinct components (or clusters) of the network. A component of a graph is the set of nodes reachable from a single node by following edges in the graph. Notice that in an (undirected) graph, the property of path connectedness is symmetric and transitive, i.e., if a node a is reachable from node b , then the inverse path also exists, and if c is reachable from a it is also reachable from b . Therefore, a component is uniquely defined by any node belonging to it. A network is said to be connected if all nodes in it belong to a single component, that is, each node is reachable from each other node.

Random graphs are locally tree-like, i.e., the number of closing a loop for a set of less than order N nodes is negligible. This also implies that below the percolation threshold, where all components (clusters) are small, almost all components are trees, i.e., posses of no loops.

To determine the percolation threshold it should be noticed that at the critical point every node reached by following a link from a previously visited node should have, on average, exactly one more link through which new nodes can be reached. If the average number of outgoing links is less than one, the uncovering process of the component will quickly decay, and only small components will be present. If the average number of outgoing links is larger than one, the size of the largest component will be proportional to that of the entire graph, i.e., a giant component, of size $O(N)$ will exist. This may lead to the conclusion that the average degree, $\langle k \rangle$, needs be two or more for a giant component to exist. However, the node reached by following a link is not chosen uniformly. The probability of reaching a node by following a link is proportional to its degree, $P_i = k_i / (N \langle k \rangle)$. The average outgoing degree of a node reached by following a link is therefore, $\sum (k-1)n(k)P_i = \langle k(k-1) \rangle / \langle k \rangle = k - 1$, where $k = \langle k^2 \rangle / \langle k \rangle$ is the ratio of the first two moments of the degree distribution. It is this quantity that should be compared to one to determine whether

a giant component exists (Cohen et al. 2000; Molloy and Reed 1995). Therefore, a giant component exists if and only if $k > 2$.

In a percolation setting the nodes or edges are removed with probability q , or, alternatively, occupied with probability $p = 1 - q$. This model may represent random failures of nodes in the network, such as random failures of routers or links in the Internet (Albert et al. 2000). The average number of outgoing links should be multiplied then by the probability, p_b , that the link is occupied, and by p_s , the probability that the node reached from the link is occupied, or not deleted. Therefore, the condition for the existence of a giant component becomes $p_b p_s (k - 1) > 1$. Alternatively, p_c , the critical site or bond percolation threshold is given by Cohen et al. (2000)

$$p_c = \frac{1}{k - 1}. \quad (2)$$

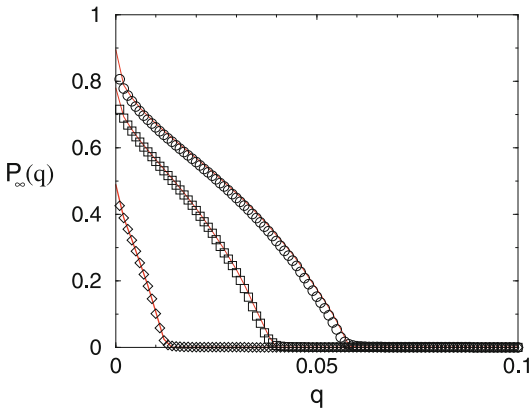
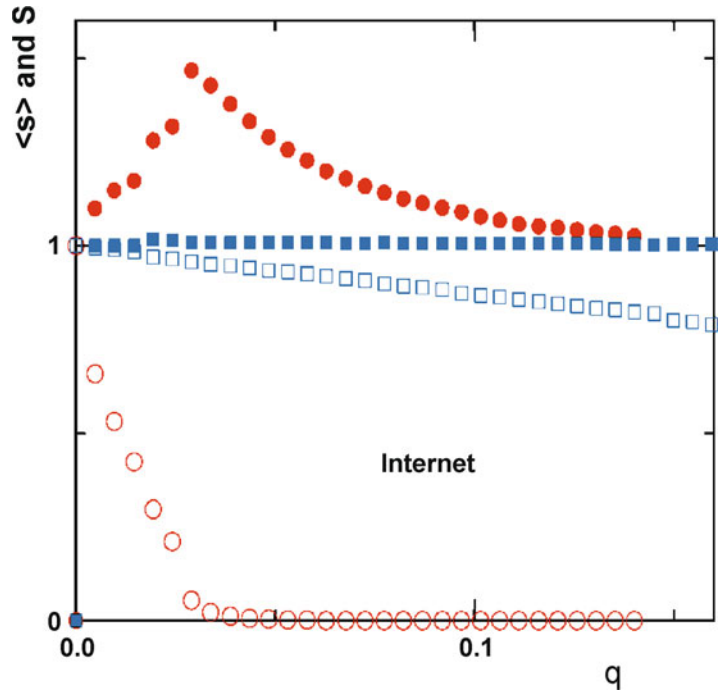
Notice that the critical threshold depends only on the first two moments of the degree distribution. Furthermore, in a scale free network with $\gamma \leq 3$ the second moment of the degree distribution diverges in the limit of infinite network size. Therefore, the critical threshold for this class of networks approaches 0, indicating that these networks are resilient to any finite fraction of random node failures (Cohen et al. 2000). Figure 1 presents the results of random node failure on the Internet as compared to an ER network.

In case the node removal is not random this situation may change drastically. The most well studied case is that of removal of the highest degree nodes, modeling an intentional, targeted attack on the most important nodes in the network. In this case calculations similar to the above lead to the conclusion that the percolation threshold is finite and small (Albert et al. 2000; Callaway et al. 2000; Cohen et al. 2001). Figure 2 illustrates the results of targeted removal of a fraction q in scale free networks.

Epidemics and Immunization

The spread of epidemics in a population can be modeled as a dynamical process in a network.

Percolation in Complex Networks, Fig. 1 Results of targeted removal of a fraction q of the nodes from an ER graph (*circles*) and a partial Internet view (*squares*). *Full symbols* represent the size of the second largest component and *empty symbols* represent P_∞ , the relative size of the largest component. (After Albert et al. (2000))



Percolation in Complex Networks, Fig. 2 The relative size of the largest component, P_∞ as a function of the fraction of targeted removed nodes, for scale free networks with $m = 1$ and $\gamma = 2.5$ (*circles*), $\gamma = 2.8$ (*squares*), and $\gamma = 3.3$ (*diamonds*). (After Cohen et al. (2001))

Each node represents an individual and the links represent interaction between individuals that allows transmission of the epidemic. Several models exist for epidemic transmission, depending on the type of epidemic. The most commonly used models are the Susceptible-Infected-Susceptible (SIS) model and the

Susceptible-Infected-Removed (SIR) model. In both models it is assumed that nodes in the susceptible state are susceptible to the epidemic, i.e., may be infected when they come in contact with an infected individual. In the infected state the individual is infected by the epidemic and may infect other individuals, and in the removed (or recovered) state the individual is no more infected or infective and also is no longer susceptible to the disease. This state may occur due to recovery from the disease while the individual remains immunized against the disease or due to death of the infected individual. The SIS model assumes that recovered individuals are again susceptible and the SIR model assumes that each individual may only be infected once in a lifetime.

In the SIS model an epidemic can either quickly decay and vanish or prevail for a long period, during which a large (finite) fraction of the population is infected. In the SIS model it was shown that in scale free networks with $\gamma \leq 3$ the epidemic always prevails, regardless of the infection rate (Pastor-Satorras and Vespignani 2001a).

Consider epidemic spreading in the SIR model. Assume each infected node infects each of its neighbors with rate R , and has a constant infection time of

T . For each neighbor, the probability of the neighbor being infected by an infected node is $p = 1 - e^{-RT}$. This can be viewed as the probability of the edge between the two nodes is occupied, i.e., can actually be used for transmission of the epidemic. Therefore, the SIR model can be mapped to a bond percolation model (Notice that in non homogeneous cases of node dependent rates a more complicated model is needed. See Newman (2002).)

The SIR model can therefore be solved by solving the bond percolation problem in the network (Grassberger 1983; Newman 2002; Sander et al. 2002). Every edge is occupied with probability p , and the epidemic can reach an endemic state (i.e., infect $O(N)$ nodes with finite probability) if $p > p_c$, and will quickly decay, infecting only a negligible portion of the population if $p < p_c$. Furthermore, the distribution of the size of the epidemic outbreak is determined by the sizes of the graph components. If a giant component exists, the probability of a single infected individual to induce an endemic state of the population is P_∞ , the size of the giant component, and the size of the outbreak is the size of the component to which this individual belongs.

To prevent epidemic outbreaks it is usually desirable to immunize the population and thus prevent the epidemic. In many cases it is difficult to immunize the entire population, and only a fraction is immunized. Each immunized individual is no longer susceptible to the disease, and can be viewed as removed from the network. The immunization process can therefore be viewed as a site percolation process, where each node is removed with probability q , or occupied with probability $p = 1 - q$. The epidemic progression can then be mapped into a site-bond percolation problem.

In order for the immunization to be highly efficient, it is desirable to surpass the percolation threshold in the immunization process, to ensure that the epidemic can not reach an endemic state. Since, as stated above, randomly immunizing a fraction of the population can be a highly inefficient process, requiring immunization of nearly 100% of the population, it has been suggested that a more efficient method for immunization is devised. The simplest such method involves the immunization of the highest degree nodes in the

population (Pastor-Satorras and Vespignani 2001b). In this case immunizing a population will require vaccinating only a finite, and relatively small, fraction of the population.

In case only partial knowledge of the population exists it is sometimes also possible to immunize the population efficiently (Dezső and Barabási 2002). However, a different method, requiring no global knowledge exists. In this method, “acquaintance immunization”, a fraction of randomly selected individuals are requested to point to one of their contacts, also randomly selected. The pointed contacts are then immunized. Although this is a seemingly random process a node having a high degree is immunized with very high probability, and the process behaves effectively as a targeted immunization of high degree nodes. See Cohen et al. (2003b) for analytical treatment and Fig. 3 for illustration of the various immunization thresholds.

The Generating Functions Method

To allow the calculation of different properties of random networks it was proposed in (Callaway et al. 2000; Newman et al. 2001) to use the generating function formalism (see, e.g., Wilf 1994). In this formalism a list of numbers A_i is treated as the coefficients of a formal power series $A(x) = \sum_i A_i x^i$. This treatment simplifies many equations regarding the variables A_i , and, in many cases, simplifies the calculation of the asymptotic behavior of the coefficients for large i .

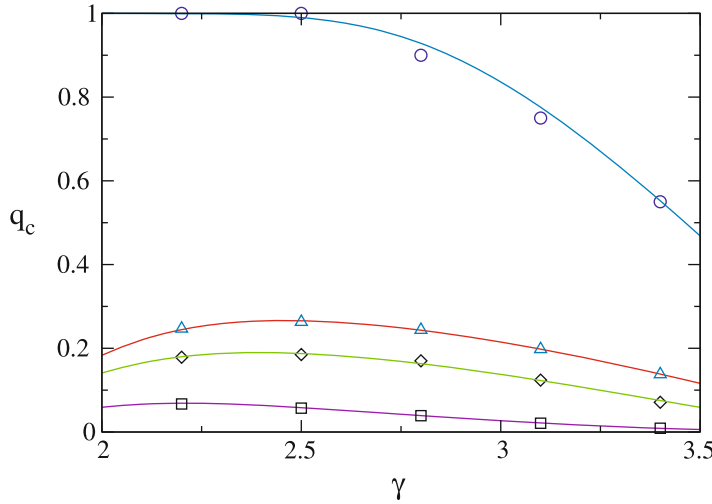
In Callaway et al. (2000) and Newman et al. (2001) a power series is built for the degree distribution,

$$G_0(x) = \sum_k P(k) x^k, \quad (3)$$

and for the distribution of outgoing links from a node reached by following a link,

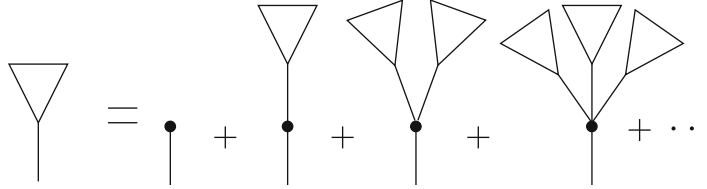
$$G_1(x) = \sum_k \frac{kP(k)}{\langle k \rangle} x^{k-1} = \frac{G'_0(x)}{G'_0(1)}, \quad (4)$$

where $G'_0 = dG_0/dx$.



Percolation in Complex Networks, Fig. 3 Critical immunization threshold, q_c , as a function of γ in scale-free networks (with $m = 1$), for the random immunization (o), acquaintance immunization (Δ), double acquaintance immunization ($\diamond$), and targeted immunization ($\square$)

strategies. Curves represent analytical results, while data points represent simulation data, for a population $N = 10^6$ (Due to the population's final size $q_c < 1$ for random immunization even when $\gamma < 3$). (After Cohen et al. (2003b))



Percolation in Complex Networks, Fig. 4 Illustration of the structure of a branch. A branch can contain either a link leading to a node with no outgoing links, or to a node

having one or more outgoing links, each leading to another branch. (After Newman et al. (2001))

A branch in the network is a link, traversed in one direction, and all the nodes reachable by following this link in this direction. This includes the node reached by following this link, and all the nodes reached by the branches emanating from the outgoing links of this node. An illustration of this recursive definition is in Fig. 4. A branch may be either finite or infinite, in which case, for a finite graph, it will reach $O(N)$ nodes and have many loops (in which case the branch description is no longer useful). A link and the node reached by following it are occupied with probability $p_b p_s$, and the generating function for the number of descendants of the reached node is G_1 . Each of the descendants is a new branch. Therefore, the generating function for the size of a branch is given by

$$H_1(x) = 1 - p_s p_b + p_s p_b G_1(H_1(x)). \quad (5)$$

A component in the graph is a node, and all the nodes reachable from it. Each of the links of a node leads to a branch. The generating function for the degree of a node is G_0 , and the probability it is occupied is p_s . Therefore, the generating function for the component size distribution is,

$$H_0(x) = 1 - p_s + p_s G_0(H_1(x)), \quad (6)$$

where H_1 is determined by Eq. (5). Again, as above, a component may be finite or infinite. Since H_0 is the generating function for the finite cluster distribution, its normalization $H_0(1)$ is the total probability that a node belongs to a finite

component, and therefore its complement $1 - H_0(1)$ is the probability that a node belongs to the giant component. Thus, the size of the giant component (that is, the fraction of nodes belonging to the giant component) is given by

$$P_\infty = 1 - H_0(1) = 1 - p_s + p_s G_0(u), \quad (7)$$

and $u = H_1(1)$ is given by the self consistent equation derived from Eq. (5)

$$u = 1 - p_s p_b + p_s p_b G_1(u). \quad (8)$$

Critical Exponents and Fractal Dimensions

Percolation problems, as well as other critical phenomena, are known to present a universal behavior near and at the critical point. That means that many properties of the critical structure behave as power laws and that near the critical point many sizes behave as powers of $p - p_c$. The universality is pronounced by the fact that the exponents in the different power laws do not depend on the microscopic details of the problem, but only on the large scale details, in particular, the dimension of the space and the symmetries. In percolation, for example, it is known that slightly above the critical point the size of the giant component behaves as $P_\infty \sim (p - p_c)^\beta$ and that the number of components of size s at criticality decays as $n(s) \sim s^{-\tau}$. Both β and τ depend only on the dimensionality and not on the microscopic details (e.g., are the same for two dimensional square and triangular lattices, etc.).

Networks can be considered infinite dimensional objects. As mentioned above, the number of nodes at a distance (number of hops) at most ℓ from a node behaves as A^ℓ for some $A > 1$. For large values of ℓ this is larger than ℓ^d , obtained for any finite dimension d . This property also leads to the impossibility of embedding networks in any finite dimension.

For percolation theory it is known (Bunde and Havlin 1996; Stauffer and Aharony 1991) that the upper critical dimension is 6, i.e., percolation on grids of any dimension larger than 6 behave

similarly to percolation in infinite dimension (also known as mean field percolation, and usually studied using the Cayley tree model (Bunde and Havlin 1996)). In mean field percolation it is known that $\beta = 1$ and $\tau = 2.5$. For dimensions less than 6 it is known that $\beta < 1$ and that $\tau < 2.5$.

To determine the critical exponents for random networks one can use the generating function formalism presented above. The size of the giant component is given by Eq. (7), where the value of u in this equation is the solution of Eq. (8). At and below the critical concentration, p_c , the size of the giant component is $P_\infty = 0$, since there are only finite components. This corresponds to a solution in which $u = 1$ and $H_0(1) = 1$. At $p = p_c + \delta$ it is expected that u is close to 1, i.e., $u = 1 - \epsilon$. Substituting this into Eq. (8) yields

$$1 - \epsilon = 1 - p_c - \delta + (p_c + \delta)G_1(1 - \epsilon). \quad (9)$$

Expanding G_1 into a power series yields

$$\begin{aligned} \epsilon &= (p_c + \delta) \\ &\times (1 - G_1(1) - G'_1(1)\epsilon - G''_1(1)\epsilon^2/2 - \dots). \end{aligned} \quad (10)$$

This equation is self consistent and gives a non trivial solution only when $p_c = G'_1(1) = 1/(k-1)$ as obtained above. The solution obtained then is $\epsilon \propto \delta$. The solution of Eq. (7) then is $P_\infty \propto \delta = (p - p_c)$, similar to infinite dimensional percolation. Using similar expansions of Eqs. (7) and (8), now at the critical point, $p = p_c$ it can be shown that the probability of a node to belong to a component of size s is proportional to, $p_s \propto s^{-3/2}$, implying that the number of components of size s behaves as $n(s) \propto s^{-5/2}$. Both these exponents are the same as obtained for infinite dimension percolation.

The above treatment is correct, however, only assuming the sums in Eqs. (7) and (8) can be expanded in a power series. This is true only if the degree distribution, $P(k)$ decays quickly enough, say exponentially. In the case of a power law degree distribution, the series expansion is incorrect, and one needs to resort to other

methods of obtaining the asymptotic behavior. The main mechanism for obtaining such asymptotics is using Abelian and Tauberian theorems. These theorems relate the decay of the coefficients of a power series and its behavior near a singular point of the function in the complex plane. Using these methods it can be shown (Cohen et al. 2003a) that the behavior of Eq. (8) near criticality becomes

$$1 - \epsilon = 1 - p_c - \delta + (p_c + \delta)(G_1(1) + G'_1(1)\epsilon + G''_1(1)\epsilon^2/2 + \dots + C\epsilon^{\gamma-1} + \dots) \quad (11)$$

Thus, when $\gamma < 3$ the nonanalytic term $C\epsilon^{\gamma-1}$ dominates the linear term, and for $3 < \gamma < 4$ it dominates the quadratic term.

In the most interesting case of $3 < \gamma < 4$ the percolation threshold is finite, as seen from Eq. (2). However, using the expansion in Eq. (11) it can be seen that near the critical point $P_\infty \propto (p - p_c)^{1/(\gamma-3)}$, so $\beta = 1/(\gamma-3)$. Similarly, it can be shown that $\tau = (2\gamma-3)/(\gamma-2)$ in this regime. Both exponents return to their mean field value for $\gamma > 4$.

Another common characteristic of critical phenomena is the fractal behavior at the critical point. For high dimensional percolation at the critical dimension $d_c = 6$ and above it is known that the fractal dimension of the largest components is $d_f = 4$. This implies that the size of the largest component behaves as $S \sim L^4$, where L is the linear dimension of the grid. Since the total grid size is $N \sim L^6$ it follows that $S \sim N^{2/3}$. Also, it is known that each branch of the components at criticality behaves as an independent random walk. Since random walks have $\ell \sim L^2$, where ℓ is the number of random walk steps, representing the distance on the fractal itself, also known as the chemical distance. This implies that $S \sim \ell^2$. This dimension, $d_l = 2$ is known as the chemical dimension (Krapivsky and Redner 2002), and since in a network no embedding space is present, and therefore L is not well defined, the chemical dimension is the most appropriate measure to be used.

To deduce the critical dimensions of a percolating network one can observe the survivability of a branch in the network. Define

$$F(x) = 1 - p_c + p_c G_1(x), \quad (12)$$

to be the degree distribution at criticality, i.e., the distribution of the number of occupied links leading to occupied nodes. Denote the number of nodes at a distance ℓ along a branch by N_ℓ . The distribution of such values can be fitted with a generating function $N_\ell(x)$. The generating functions for different layers satisfy

$$N_{\ell+1}(x) = F(N_\ell(x)). \quad (13)$$

At criticality the average number of nodes on the ℓ th layer along a branch is 1, since a lower branching factor will lead to fast extinction of all branches, and a higher branching factor will give an infinite branch with a high probability. Therefore, the number of nodes at a distance ℓ only along branches that survive at least ℓ layers equals the average number of nodes in the ℓ th layer, which is 1, divided by the fraction of branches surviving at least ℓ layers. This number can be obtained by noticing that the probability of a branch to become extinct at the first ℓ layers is given by $N_\ell(0)$, the probability of having 0 nodes in the ℓ th layer. The average number of nodes at the ℓ th layer of surviving branches is therefore $m_\ell = 1/(1 - N_\ell(0))$, and the fractal dimension can be obtained from the total number of nodes up to the ℓ th layer in surviving branches, $M_\ell = \sum_{i=1}^{\ell} m_i$. The asymptotic behavior of $N_\ell(0)$ can again be obtained and leads to $M_\ell \propto \ell^{(\gamma-2)/(\gamma-3)}$ for $3 < \gamma < 4$ and $M_\ell \propto \ell^2$ for $\gamma > 4$ and for ER networks. This implies

$$d_l = \begin{cases} \frac{\gamma-2}{\gamma-3}, & 3 < \gamma < 4, \\ 2, & \gamma > 4. \end{cases} \quad (14)$$

The size of the largest component at criticality can be obtained using the other critical exponents. As presented above, the asymptotic behavior of

the component size distribution is $P(s) = s^{-\tau+1}$, where $P(s)$ is the probability of a node to belong to a component of size s . There are N nodes in the graph, and therefore it is expected that the size of the largest component of a graph, S , will be such that $P(S) \sim N^{-1}$. This leads to $S \sim N^{1/(\tau-1)}$ and to

$$S \propto \begin{cases} N^{(\gamma-2)/(\gamma-1)}, & 3 < \gamma < 4, \\ N^{2/3}, & \gamma > 4. \end{cases} \quad (15)$$

Optimal Paths and Minimum Spanning Trees

Communication in a network usually follows the shortest path from source to destination. The network structure and function usually depends only weakly on the space the network exists in. Hence, the path length is usually defined by the intrinsic properties of the network. The simplest definition of the path length between two nodes, a and b , in a network is the hop distance, i.e., the minimum number of links that need to be traversed in order to arrive from a to b . The average path length in networks has been studied extensively, and is known to be logarithmic in the size of the network for ER (Bollobás 1985) and scale free graphs with $\gamma > 3$ (Newman et al. 2001) and of order $\log \log N$ in scale free graphs with $\gamma < 3$ (Cohen and Havlin 2003).

Another definition for the distance in a network can be given in case each link has some intrinsic length, or some intrinsic property (similar to energy in physics), termed “weight”, measuring the cost of using it. When the link length distribution is narrow (the “weak disorder” limit) the behavior of the optimal (lowest cost) path is expected to be very similar to that of the shortest path. However, when the distribution of link costs becomes very wide (the “strong disorder” limit) the behavior of the optimal path becomes very different from that of the shortest path (Cohen et al. 2003a; Wilf 1994).

The limit of strong disorder is observed clearly when the weight distribution is so wide, that the weight of each link is expected to be at least twice

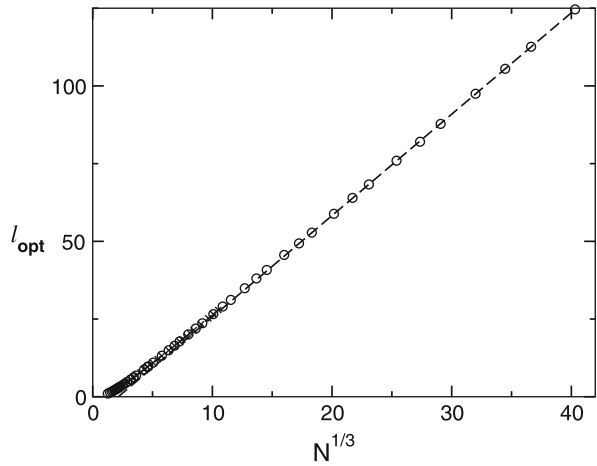
as large as the next highest link weight. This implies also that the weight of each link is larger than that of *all* links with lower weight. In this case paths can be compared by sorting the link weights along each path, and then comparing the lists of link weights by lexicographic order. It should be noted that the graph of all shortest paths also called “optimal paths” is a tree, i.e., has no loops. It is similar to the minimum spanning tree (MST), which presents the same behavior regardless of the weight distribution. Another similar case is high bandwidth information transmission in communication networks, where it may be desirable to transmit through the path having the highest *minimal* bandwidth, to avoid bottlenecks.

An alternative method for reaching the optimal path tree is the bombarding method. In this method the links in the network are removed one by one by order of decreasing weight. It is clear that removing a high weight link will not change any of the optimal paths, unless it makes the network disconnected, in which case it is not removed. Since the order of the link weights is random, so is the order of removal, and therefore this model is identical to random percolation, with the difference of refraining from removing links that make the network disconnected. Since at criticality percolation disintegrates the network into a collection of trees (or almost trees), the critical percolation component (cluster) is a subgraph of the optimal path tree.

This mapping of the optimal path and minimum spanning tree to a (restricted) percolation problem is very useful, since it allows the determination of the properties of these objects, based upon their similarity to the network at the critical point. From the results above in section “Critical Exponents and Fractal Dimensions” the size of the largest component in ER networks is $S \propto N^{2/3}$. The chemical dimension is $d_l = 2$. Therefore, $S \propto \ell^2$, leading to the average hop distance between nodes on the critical components being $\ell \propto N^{1/3}$. Similarly for scale free networks with $3 < \gamma < 4$, $\ell \propto N^{(\gamma-3)/(\gamma-1)}$. This presents a lower bound on the length of the optimal path in ER and scale free networks (Braunstein et al. 2003). In fact, it is observed that the critical components are

Percolation in Complex Networks, Fig. 5

The optimal distance l_{opt} as a function of $N^{1/3}$ for ER graphs with strong disorder. (After Braunstein et al. (2003))



connected in a compact way i.e., through a small number of components in the optimal path tree (or MST) and this lower bound is actually exact. See Fig. 5.

Fragmentation of Social Networks

One of the most interesting questions in sociological networks is quantifying the collapse process of a network. Under certain circumstances it may happen that a network of friendship or acquaintance is fragmented into several components. It is desirable in many cases to quantify the fragmentation using a measure that is sensitive to the different possible partitions into fragments. Such a measure, developed in Borgatti (2006) can distinguish between different partitions of a network, based on the sizes of all components. This is especially important in small and medium size networks, and in non random fragmentation processes, where the fragments may contain several similarly sized components.

Notice that the phenomenon of network fragmentation due to link removal (acquaintance separation) or node removal (individuals leaving the social network) is similar to bond and site percolation, respectively. One of the main shortcomings of the percolation description in this case is the focus of percolation theory on random processes and in the limit of large system size (the “thermodynamic limit”). Here we will discuss the

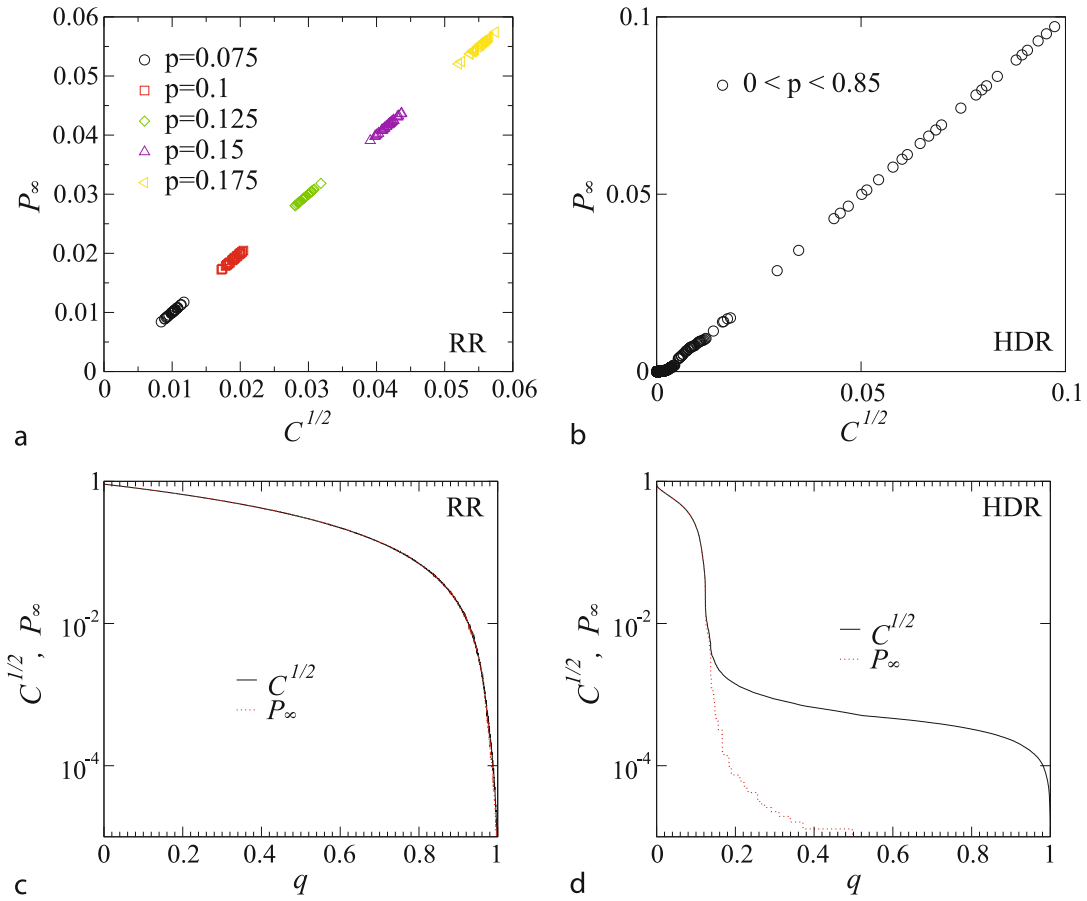
proposed fragmentation measure and its relation to the standard percolation measures.

The suggested measure of fragmentation, F , is the number of pairs of nodes not reachable from each other, divided by the total number of pairs in the network (Borgatti 2006). Since nodes that are reachable from each other belong to the same component, this is equivalent to the following definition:

$$F = 1 - \frac{\sum_{i=1}^n s_i(s_i - 1)}{N(N - 1)} \equiv 1 - C, \quad (16)$$

where s_i is the size of the i th component and n is the number of components in the graph.

In Chen et al. (2007) the relation between percolation theory and this fragmentation measure was studied. As discussed above, in the limit of $N \rightarrow \infty$ above the percolation threshold there is a large gap between the size of the giant component, which is of order N and the size of the second largest component, which is usually of logarithmic size. At the threshold, the size of the largest component is of order $N^{2/3}$ for ER networks and some power of N for scale free networks, and the component size distribution is continuous. Below the percolation threshold the distribution is continuous again. However, the size of the largest component is even smaller (logarithmic in ER networks). Equation (16) therefore can be presented in the following equivalent form in the limit of large N



Percolation in Complex Networks, Fig. 6 Comparison of P_∞ and $C = 1 - F$ for random removal (a, c) and high degree removal (b, d) of links in a real social network of working relations in Sweden. (After Chen et al. (2007))

$$F \approx 1 - P_\infty^2 - \frac{\sum_s n(s)s(s-1)}{N^2} \approx 1 - P_\infty^2 - \frac{\langle s \rangle}{N}. \quad (17)$$

Notice that $\langle s \rangle$ represents the average component sampled over all nodes, rather than over all clusters. This gives a larger weight to larger components. In fact, since $\tau = 2.5$ in ER networks, and $\tau < 3$ for all $\gamma > 3$ and that $P(s)$, the probability of a node to belong to a component of size s scales as $P(s) \sim s^{-\tau+1}$, it follows that $\langle s \rangle$ diverges similarly to S at the threshold.

For finite networks in particular F has the advantage that it presents some measure of the fragmentation process both above and below the critical threshold. A comparison of P_∞ and F as measures of fragmentation can be seen in Fig. 6.

Future Directions

Different types of percolation can be defined and studied on random networks. Random percolation has special features in terms of the threshold and the critical exponents in scale free networks. The percolation theory of networks has many applications in epidemiology, network robustness, social networks analysis, and communication network efficiency.

Several open questions still remain regarding percolation theory in networks and its applications. For scale free networks with $2 \leq \gamma \leq 3$ it seems that a phase transition still exists with a threshold that approaches zero as a function of N . Although some progress has been made in this direction (see, e.g., Lee et al. 2004), the nature of this transition is not completely well

understood and understanding it may enable the understanding of properties such as the optimal path behavior in such networks (which, from numerical results, seems to behave logarithmically).

Other important topics, which are not yet fully understood, is the question of optimal network design, and optimized attack strategies. In optimal network design, an attempt is made to find the parameters (such as degree distribution, correlations, or clustering) that produce a network class, with optimal percolation properties, including minimum random or targeted percolation thresholds, good near critical behavior, etc. Optimized attack strategies attempt to bring the network to the percolation threshold (or any other desired point) with the minimum number of removed nodes or links. Targeted attacks are usually very efficient in achieving percolation. However, more efficient methods can be conceived.

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